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Alkyl complexes of divalent lanthanides and heavy alkaline earth metals

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The review presents data on the synthesis, structure, reactivity, and catalytic activity of alkyl derivatives of rare earth metals in the oxidation state +2 (Sm, Eu, Yb) and their analogues containing heavy alkaline earth metals (Ca, Sr, Ba). The synthetic aspects and structural features of this unique class of organometallic compounds, which contain highly reactive M–C bonds, including alkyl, α-silylmethyl, and also benzyl, diphenylmethyl, and triphenylmethyl derivatives are considered. The bibliography includes 157 references.

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1. Introduction

Over the past two decades, alkyl derivatives of rare earth and heavy alkaline earth metals have been the focus of sustained attention due to their unique reactivity.[1–3] Tremendous advances were made in the investigation of alkyl compounds of rare earth metals in an oxidation state of +3,[4–12] which demonstrated amazing potential in a variety of important and challenging stoichiometric and catalytic reactions, such as activation of C–H bonds,[13–23] functionalization of alkanes,[24–27] polymerization,[12,28–33] and hydrofunctionalization of unsaturated substrates.[34–45] At the same time, alkyl complexes of rare earth metals in an oxidation state of +2 still remain poorly studied despite their unique chemical properties resulting from the presence of two reactive centres in these compounds, namely, Ln(II) redox-active centre and the Ln–C bond. The ions of 'classical' lanthanides, which are characterized by a stable divalent state, have radii (Yb^{2+} [1.02 Å], Sm^{2+} [1.15 Å], Eu^{2+} [1.14 Å]; CN 6)[46,47] close to those of the M^{2+} ions of heavy alkaline-earth metals (Ca^{2+} [1.00 Å], Sr^{2+} [1.18 Å]; CN 6),[46] and their homotypic compounds have striking similarity in structures and reactivity.[48] Apart from close values of the ionic radii, the similarity between the chemical properties of Ln(II) and heavy alkaline-earth metal derivatives is also defined by the similarity between other properties such as electropositivity of these metals and predominant ionic component in a metal–organic ligand interaction. Moreover, in contrast to d-metal complexes, in Ln(II) complexes, due to the limited radial extension of f orbitals, their overlap with the ligand orbitals does not significantly affect the interaction, structure, and chemical properties of the resulting compounds. Therefore, for the compounds of electropositive Ln(II) and M(II), metal–ligand interaction and the structure of complexes are mainly determined by electrostatic and steric effects.

For a long time, progress in the synthesis of alkyl derivatives of divalent rare earth metals was constrained by many factors, such as the difficulty of stabilizing the coordination sphere of large and electropositive M(II) ions,

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instability of their compounds towards β-hydride elimination, and, consequently, low thermal stability. To circumvent these issues and to make possible the synthesis of thermally stable compounds, kinetic stabilization of alkyl derivatives through the steric and coordination saturation of the M(II) sphere should be provided. A possible approach to stabilizing alkyl derivatives is their substitution with bulky silylmethyl ligands $C(SiMe_3)_3$ or $CH(SiMe_3)_2$, which have no hydrogen β-atoms, thereby blocking the very possibility of the β-hydride elimination. The use of alkyl ligands containing covalently linked donor groups ([$C(SiMe_3)(SiMe_2OMe)$], [$Me_3SiCH(C_6H_4)NMe_2$], [$C(SiMe_3)_2(SiMe_2CH{=}CH_2)$]), which can form coordination bonds with M(II), also stabilizes the metal complexes. In benzyl and diphenylmethyl complexes, the stabilization can be achieved due to the delocalization of the negative charge over the conjugated π-system and through non-bonded M(II) – arene interaction. Moreover, it was shown that non-bonded β-SiH-agostic interactions of Ln(II) ions with [$C(SiHMe_2)_3$] groups are also an effective means of stabilizing the alkyl derivatives.

Particular challenges in the synthesis of the mixed-ligand M(II) alkyl derivatives arise from their pronounced tendency to the ligand redistribution and the Schlenk equilibrium due to the high degree of ionic character of the bonds between the metal and an organic ligand.[49 – 52] This reaction can generally be suppressed by the use of sterically demanding polydentate stabilizing ligands.

A number of works published over the past decade have demonstrated an impressive catalytic potential of alkyl derivatives of Ln(II) and also of Ca, Sr, and Ba, which proved to be effective catalysts of the C – C and C – E (E = Si, N, P) bond formation, polymerization, and hydrogenation of alkenes. The present review provides data on the synthesis, structure, reactivity, and catalytic activity of alkyl derivatives of the rare earth metals in +2 oxidation state and their analogues containing heavy alkaline earth metals.

2. Complexes of Ln(II) and heavy alkaline earth metals bearing alkyl ligands

Unlike alkyl- and arylmagnesium halides, obtained by Grignard *via* a straightforward synthesis over a hundred years ago, much less attention was given to the organometallic chemistry of heavier alkaline earth metals and divalent lanthanides.[49, 53 – 57]

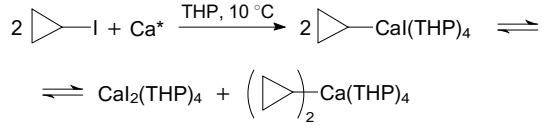
The first attempts to obtain dimethyl complexes of alkaline earth metals were undertaken by Payne and Sanderson[58] as early as in 1958. The authors reported that homoleptic dimethyl complexes Me_2M (M = Ca, Sr, Ba) can be obtained by the reaction of MeI with metals in anhydrous pyridine (Py). During the subsequent multiple recrystallizations of the products, symmetrization of the initially generated methyl iodide derivatives $MeMI(Py)_n$ and the formation of Me_2M and $MI_2(Py)_n$, respectively, occurred. The formation of dimethyl derivatives was confirmed indirectly by measuring the volume of CH_4 released during hydrolysis of the resulting compounds.

Later, the synthesis of alkylcalcium halides RCaHal obtained in THF or Et_2O solutions by treating the calcium metal with haloalkanes RX (R = Me, Et, Pr^n, Bu^n, n-C_5H_{11}; X = Cl, Br, I) was described.[59] Reactivity of haloalkanes was shown to decrease along the series of RI > RBr > RCl. With the most active iodoalkanes RI, the reaction occurred even at a low temperature (−50 to −35 °C), while the use of chloro-substituted analogues required the reaction to be carried out at an elevated temperature (35 – 65 °C). However, the obtained alkylcalcium halides MeCaX (X = Br, I), EtCaX (X = Cl, Br, I), Pr^nCaI, Bu^nCaX (X = Cl, Br, I), n-$C_5H_{11}CaI$ were not isolated in the individual state, and their formation was confirmed indirectly through identification of alkane RH formed during hydrolysis.

The first attempts to synthesize lanthanide analogues of the Grignard reagent were made by Evans *et al.*[60] in 1971. The treatment of lanthanide metals Ln^0 (Ln = Eu, Yb) with haloalkanes RI (R = Me, Et) in THF solution at low temperature afforded the corresponding alkyl halide derivatives of the $RLn^{II}I$ type (R = Me, Ln = Yb; R = Et, Ln = Eu, Yb). The composition of the resulting compounds was confirmed by the elemental analysis data and by the reactions typical of the Grignard reagents. Thus, compounds $RLn^{II}I$ gave positive tests with Michler's ketone, and the treatment of MeYbI with dimethylphenylchlorosilane $PhSiMe_2Cl$ furnished $PhSiMe_3$.

Recently, attempts to obtain cyclopropyl calcium complex *via* the treatment of activated calcium with cyclopropyl iodide in tetrahydropyran (THP) have been reported.[52] However, due to the establishment of the Schlenk equilibrium, the reaction was accompanied by the formation of a homoleptic derivative (cyclo-Pr)$_2$Ca(THP)$_4$ and precipitation of $CaI_2(THP)_4$. The authors failed to isolate both cyclopropyl iodide complex (cyclo-Pr)CaI(THP)$_n$ and bis(alkyl) derivative (cyclo-Pr)$_2$Ca(THP)$_4$ (Scheme 1).

Scheme 1

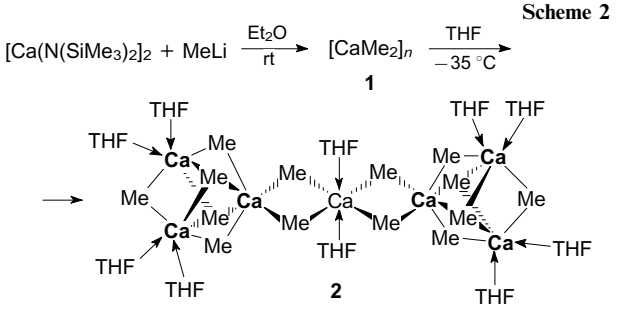


THP is tetrahydropyran

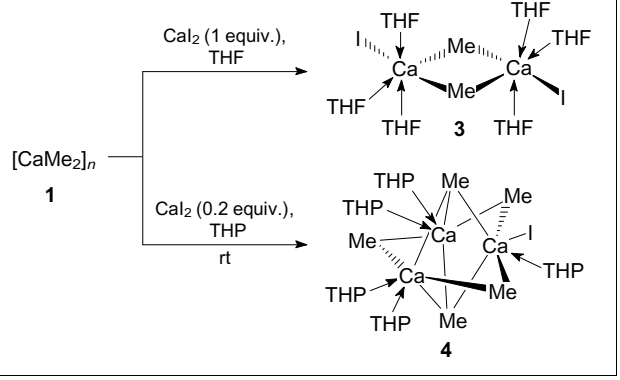
In 2018, Wolf *et al.*[61] demonstrated that the reaction of $Ca[N(SiMe_3)_2]_2$ with MeLi in Et_2O led to the precipitation of $[CaMe_2]_n$ (**1**), the low solubility of which is most likely due to its polymeric structure. Dissolution of **1** in THF enabled the isolation and crystallographic characterization of dimethyl heptanuclear complex $[Ca_7Me_{14}(THF)_{10}]$ (**2**) (Scheme 2).

Also, it was shown that the reaction of $[CaMe_2]_n$ (**1**) with anhydrous CaI_2 is a convenient procedure to obtain analogues of the Grignard reagent.[61] In this case, reactants react in different ratios depending on the nature of the solvent. Thus, in THF, compound **1** and CaI_2 react in equimolar amounts to give a dimeric complex $[(THF)_3Ca(\mu\text{-}Me)I]_2$ (**3**), whereas in THP, **1** reacts with

Scheme 2



Scheme 3

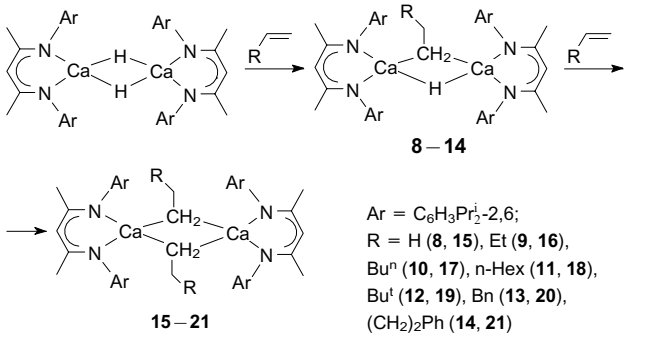


CaI_2 only in a 5 : 1 ratio, affording trinuclear complex $(THP)_5Ca_3(\mu\text{-}Me)_5I$ (**4**) (Scheme 3). The structures of complexes **3** and **4** were confirmed by the X-ray diffraction analysis. It is notable that for methyl iodide derivatives **3** and **4**, the formation of di- and trinuclear structures occurs due to the bridging methyl groups.

Wolf *et al.*[61] used complex **1** as a starting compound in the synthesis of heteroleptic methyl calcium complexes $[Tp^{Bu^t,Me}]CaMe(Solv)$ [Solv = THF (**5**), THP (**6**)] (Scheme 4), containing tris(pyrazolyl)borate ligands ($[Tp^{Bu^t,Me}]$). It was shown that the treatment of complex **1** with an equimolar amount of $[Tp^{Bu^t,Me}]H$ in THF or THP leads to protonolysis of methyl groups with the elimination of CH_4 and formation of complexes **5** and **6**. With two molar equivalents of TpH, the reaction with complex **1** affords homoleptic complex $[Tp^{Bu^t,Me}]_2Ca$ (**7**). The authors point out that heteroleptic complexes **5** and **6** are stable in aromatic and ethereal solvents and do not undergo symmetrization. Moreover, mixing the equivalent amounts of compounds **1** and **7** in THF immediately gives heteroleptic methyl complex **5**.

It was demonstrated that alkyl derivatives of Ca and Sr could be obtained by treating alkenes with the corresponding hydrides.[62 – 65] Dimeric calcium hydride complex $\{[BDI]Ca(\mu\text{-}H)\}_2$, bearing β-diketoiminate ligand $[(Pr^i_2C_6H_3)N{=}C(Me)CHC(Me){-}NH(C_6H_3Pr^i_2)]$ (BDI), reacts with terminal alkenes to give a series of heteroleptic alkyl complexes **15** – **21** (Scheme 5).[62 – 64] Reaction monitoring by NMR spectroscopy indicated the sequential insertion of two alkene molecules into Ca – H bonds of dimeric hydride $\{[BDI]Ca(\mu\text{-}H)\}_2$. Alkyl hydride complexes **8** – **14** formed in the first step gradually reacted with the second equivalent of alkene to afford dimeric alkyl derivatives

Scheme 5



15 – **21**. The authors noted that calcium hydride complex $\{[BDI]Ca(\mu\text{-}H)(THF)\}_2$, containing THF molecules in the coordination sphere of the metal, is unreactive towards alkenes. Using the similar protocol, the first dimeric ethyl strontium complex $\{[BDI^{DIPeP}]Sr(\mu\text{-}Et)\}_2$ (**22**), containing β-diketoiminate ligand $[BDI^{DIPeP}]$ with bulky 2,6-diisopentylphenyl substituents at the nitrogen atoms, was obtained and crystallographically characterized.[65]

The structures of complexes $\{[BDI]Ca(\mu\text{-}CH_2CH_2R)\}_2$ (**14** – **21**) and $\{[BDI^{DIPeP}]_2Sr(\mu\text{-}Et)\}_2$ (**22**) were confirmed by X-ray diffraction analysis to show that they are dimers due to the presence of bridging alkyl groups.[62, 64, 65] Bonding patterns of alkyl groups located inside the planar centrosymmetric four-membered M_2C_2 under differ significantly (Table 1). Each of the metal atoms is bonded to the α-C atom of one alkyl group [Ca – α-C, 2.474(2) – 2.507(2) Å; Sr – α-C, 2.713(2) Å], and also to α- and β-carbons of the second alkyl ligand [Ca – α-C, 2.563(2) – 2.595(2) Å; Ca···β-C, 2.737(2) – 2.840(2) Å; Sr – α-C, 2.798(2) Å; Sr···β-C, 3.034(2) Å].

A similar reaction of calcium hydride complex $\{[BDI]CaH\}_2$ with 1,5-hexadiene proceeds to give dimeric calcium complex **23**, containing cyclopentamethyl moiety, which is formed *via* the intramolecular cyclization (Scheme 6).[63] Reaction monitoring by NMR spectroscopy confirmed the sequential insertion of the alkene into Ca – H bonds. In the case of 1,7-octadiene, the reaction of hydride complex $\{[BDI]CaH\}_2$ leads to the insertion of only one of the multiple bonds of 1,7-octadiene to afford alkyl complex **24** containing bridging alkyl ligands with a terminal double bond, without subsequent cyclization.[64]

Rösch *et al.*[65] also studied the reactivity of hydride complex $\{[BDI]CaH\}_2$ towards the internal C=C bond of norbornene. The authors succeeded to obtain stable alkyl

Scheme 4

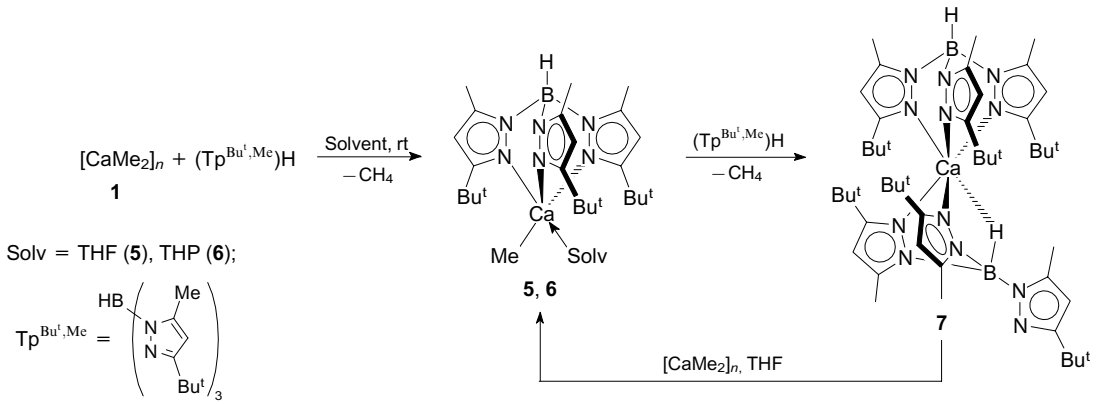
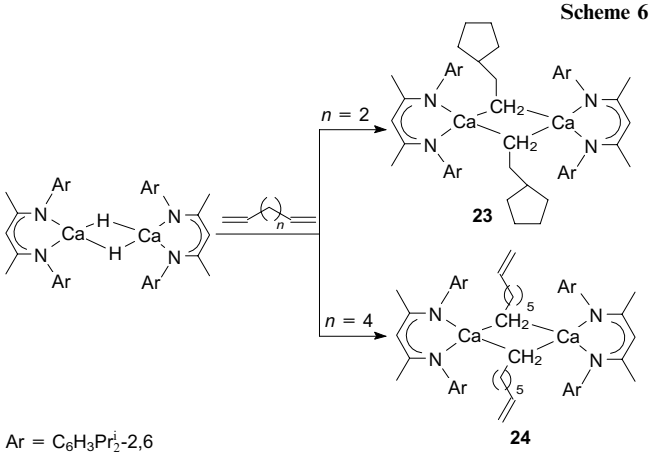


Table 1. Selected interatomic distances (Å) in heteroleptic alkyl complexes $\{[L]M[R]\}_n$.

Complex	M – α-C	M···α-C	M···β-C	M···M	Ref.
$\{[BDI]Ca(\mu\text{-}CH_2Me)\}_2$ (**15**)	2.485(2)	2.573(2)	2.840(2)	3.340(1)	62
$\{[BDI]Ca[\mu\text{-}CH_2(CH_2)_2Me]\}_2$ (**16**)	2.499(2)	2.579(2)	2.802(2)	3.291(1)	62
$\{[BDI]Ca[\mu\text{-}CH_2(CH_2)_4Me]\}_2$ (**17**)	2.491(2)	2.582(2)	2.760(2)	3.325(1)	62
$\{[BDI]Ca[\mu\text{-}CH_2(CH_2)_6Me]\}_2$ (**18**)	2.498(2)	2.571(2)	2.752(2)	3.326(1)	64
$\{[BDI]Ca[\mu\text{-}CH_2CH_2CMe_3]\}_2$ (**19**)	2.507(2)	2.595(2)	2.737(2)	3.338(1)	64
$\{[BDI]Ca[\mu\text{-}CH_2(CH_2)_2Ph]\}_2$ (**20**)	2.492(2)	2.577(2)	2.809(2)	3.340(1)	64
$\{[BDI]Ca[\mu\text{-}CH_2(CH_2)_3Ph]\}_2$ (**21**)	2.474(2)	2.563(2)	2.751(2)	3.308(1)	64
$\{[BDI]Ca[\mu\text{-}CH_2\text{-cyclo-}C_5H_9]\}_2$ (**23**)	2.517(2)	2.576(2)	–	3.342(1)	63
$\{[BDI]Ca[\mu\text{-}CH_2(CH_2)_5CH{=}CH_2]\}_2$ (**24**)	2.471(2)	2.562(2)	2.721(2)	3.328(1)	64
$\{[BDI]Ca\}_2(\mu\text{-}H)[\mu\text{-}CH(C_6H_{10})]$ (**25**)	2.469(2)	2.619(2)	–	3.384(1)	64
$\{[BDI^{DIPeP}]_2Sr(\mu\text{-}Et)\}_2$ (**22**)	2.713(2)	2.798(2)	3.034(2)	3.617(1)	65
$[Tp^{Ad,Pr^i}]Ca[CH_2(CH_2)_3Ph](THP)$ (**27**)	2.515(2)	–	3.542(2)	–	66

Scheme 6

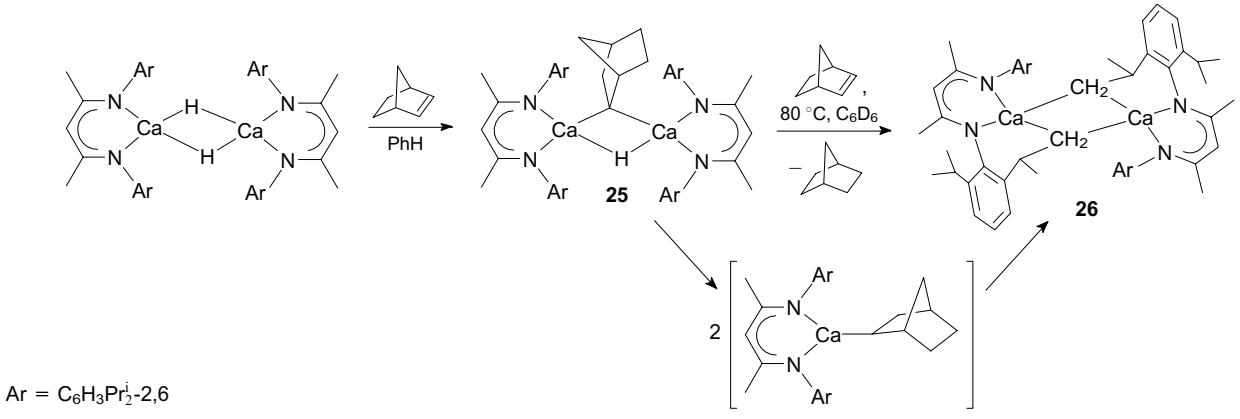


hydride calcium complex **25** containing μ^2-bicyclo[2.2.1]hept-2-yl ligand along with a bridging μ^2-hydride one (Scheme 7). However, upon the addition of the second equivalent of norbornene to complex **25** at 80 °C in benzene, the intramolecular activation of Me groups of isopropyl substituent in β-diketoiminate ligand takes place, leading to the formation of novel dimeric complex $\{[BDI^{-H}]Ca\}_2$ (**26**) and elimination of alkane. The authors suggest this reaction to proceeds *via* an intermediate monomeric calcium alkyl complex [BDI]Ca[CH(C_6H_{10})] containing terminal bicyclo[2.2.1]hept-2-yl ligand, which immediately deprotonates Me group with the elimination of bicyclo[2.2.1]heptane. The structures of complexes **25** and **26** were confirmed by X-ray diffraction analysis (see Table 1).

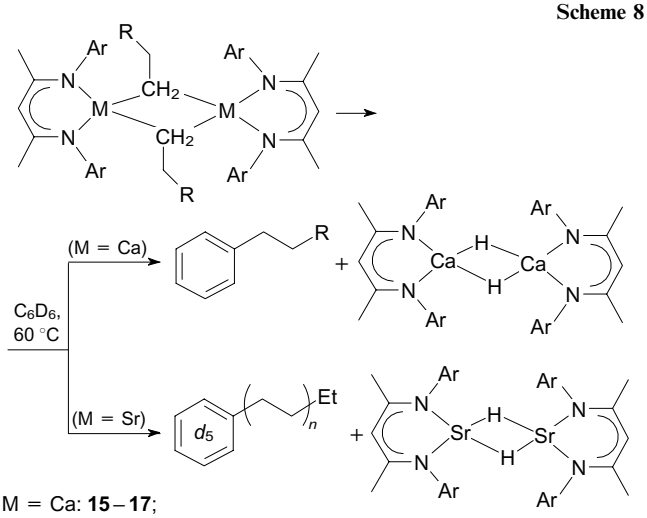
Calcium β-diketoiminate complexes $\{[BDI]Ca(\mu\text{-}CH_2CH_2R)\}_2$, containing bridging alkyl ligands, have demonstrated unique reactivity, allowing for the nucleophilic substitution in the benzene ring.[62,63] Dissolution of these complexes in benzene or in its deuterated analogue C_6D_6 results in the replacement of one of the H(D) atoms with an alkyl group. This reaction provides alkylated benzenes ($RCH_2CH_2C_6(H/D)_5$) and calcium hydride complex $\{[BDI]_2Ca(\mu\text{-}H)\}_2$ (Scheme 8). The authors pointed out that for calcium complexes **15**–**17**, only nucleophilic substitution in the benzene ring was observed, whereas ethylene oligomers were not formed even at elevated temperature (60 °C). In constrast, the reaction of strontium complex **22** $\{[BDI^{DIPeP}]Sr(\mu\text{-}Et)\}_2$ with ethylene in benzene solution involved competing ethylene insertion into the Sr – C bond and nucleophilic substitution in the benzene ring to produce a mixture of alkylated benzenes $Et(CH_2CH_2)_nC_6D_5$ (n = 1, 2, 3, *etc.*).[65] According to the DFT calculations, the intermediate step of alkylation of benzene with highly nucleophilic calcium and strontium complexes provided a non-activated Meisenheimer complex.[62,65]

Insertion of a terminal alkene $Ph(CH_2)_2CH{=}CH_2$ into the Ca – H bond of monomeric calcium hydride complex $[Tp^{Ar,Pr^i}]CaH(THP)$, containing a bulky tris(pyrazolyl)borate ligand (Tp), proceeds in a similar way to afford the corresponding alkyl derivative $[Tp^{Ar,Pr^i}]Ca[CH_2(CH_2)_3Ph](THP)$ (**27**) (Scheme 9). Due to a larger volume of the Tp^{Ar,Pr^i} ligand as compared to BDI,

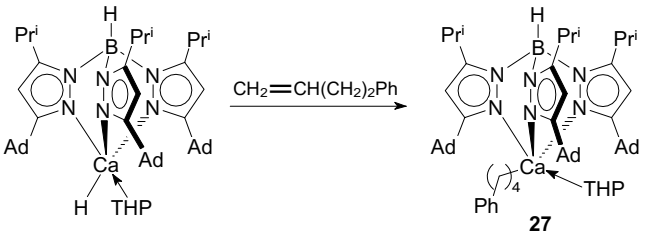
Scheme 7



Scheme 8



Scheme 9



compound **27** is monomeric. Despite the fact that the alkyl ligand $[CH_2(CH_2)_3Ph]$ in **27** is terminal, the Ca – C bond length [2.515(2) Å] is comparable to those in dimeric complexes **15** – **24** containing bridging alkyl groups (see Table 1). No interaction of the calcium ion with β-CH_2 group is observed in complex **27** [Ca···β-C 3.542(2) Å].

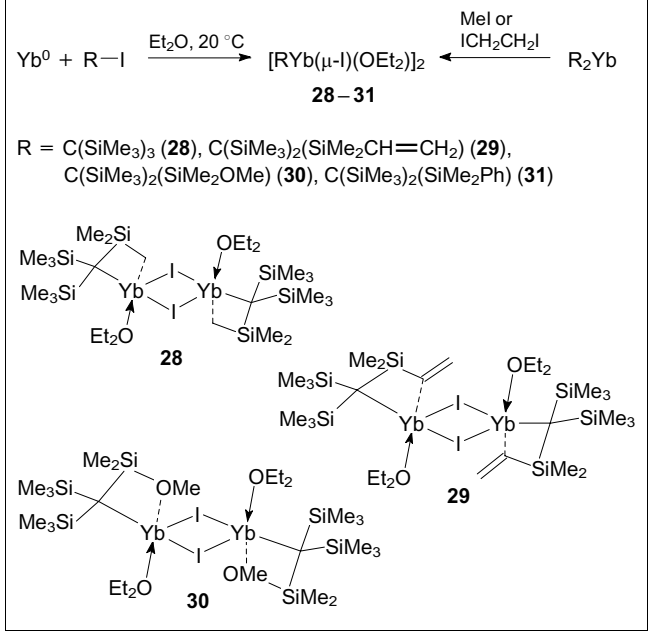
3. Complexes of Ln(II) and heavy alkaline earth metals containing α-silylmethyl ligands

Chemistry of alkyl derivatives of divalent lanthanides and alkaline earth metals experienced dynamic growth in the mid-1990s due to the use of bulky α-silyl-substituted carbanions as alkyl groups. Advances in the synthesis of bis(alkyl) derivatives of α-silyl-substituted methanes stem primarily from the absence of β-hydrogen atoms in these moieties, which rules out the possibility of β-hydride elimination. Also, the presence of bulky substituents provides good solubility even in non-polar solvents and hampers the formation of associates. At the same time, changing the number of silyl groups at the methanide carbon atom and the introduction of donor atoms into the alkyl ligand allows varying its steric and coordination capabilities within wide limits.[67]

3.1. Alkyl halide complexes

Eaborn *et al.*[68, 69] reported the first crystallographically characterized Yb(II) analogues of Grignard reagents bearing bulky silyl-substituted alkyl ligands in 1994 – 1996. It was shown that treating the Yb metal with alkyl iodides

Scheme 10



$IC(SiMe_3)_2(SiMe_2X)$ leads to the corresponding alkyl iodide derivatives of Yb(II) **28** – **31** (Scheme 10).

The authors noted that these compounds were also formed under the action of iodoalkanes MeI or $I(CH_2)_2I$ on the corresponding bis(alkyl) complexes of divalent ytterbium R_2Yb.

According to the X-ray diffraction data, complexes **28** – **30** are dimeric due to the presence of two bridging iodide ligands linking two metal centres to form a planar four-membered ring Yb_2I_2 (Table 2). It should be emphasized that non-bonded interactions between Yb(II) ions and α-carbons of the vinyl group of the alkyl ligand were found in complex **29**, as confirmed by a rather short Yb···C(H) distance [2.98(2) Å].

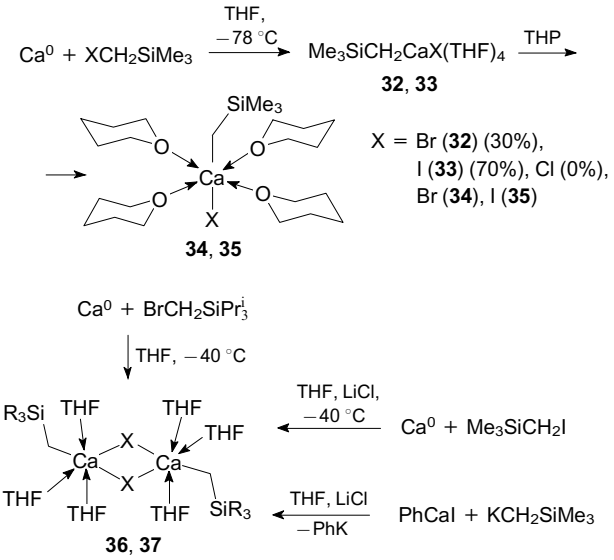
Alkyl iodide derivatives of Yb(II) are unstable in solution and undergo symmetrization. Thus, being dissolved in toluene-d_8, complexes **28** – **31** transform into the corresponding bis(alkyl) complexes $Yb[C(SiMe_3)_2(SiMe_2X)]_2$ with the precipitation of YbI_2.

Later, Westerhausen and co-workers [52, 70] obtained and structurally characterized a series of alkylcalcium halide complexes $(R_3SiCH_2)CaX(Solv)_n$ (X = Cl, Br, I; R = Me, Pr^i; Solv = THF, THP) (Scheme 11). Activated calcium metal reacted with alkyl halides XCH_2SiMe_3 in THF to give the corresponding alkylcalcium iodide complexes $(Me_3SiCH_2)CaX(THF)_4$ [X = Br (**32**), I (**33**)]. As a result of subsequent treatment of **32** and **33** with tetrahydropyran, monomeric alkylcalcium halides $[Me_3SiCH_2)CaX(THP)_4$ (X = Br (**34**), I (**35**)] were obtained and structurally characterized. In the reaction of bulkier bromo-derivative $BrCH_2SiPr^i_3$ with activated calcium, the formation of a dimeric alkyl bromide complex $[(Pr^i_3SiCH_2)Ca(THF)_3(\mu\text{-}Br)]_2$ (**36**) was observed. The authors noted that the halogen nature had a dramatic impact on the yields of alkyl halide derivatives. Thus, for the most active iodoalkane ICH_2SiMe_3, the yield of the corresponding alkylcalcium iodide **33** was 70%, and for its bromo analogue **32**, the yield was 30%. Under the above conditions, $ClCH_2SiMe_3$ did not react with calcium metal. Alkyl chloride complex $[(Me_3SiCH_2)Ca(THF)_3(\mu\text{-}Cl)]_2$ (**37**) was synthesized *via* the reaction of calcium metal with ICH_2SiMe_3 in THF in the

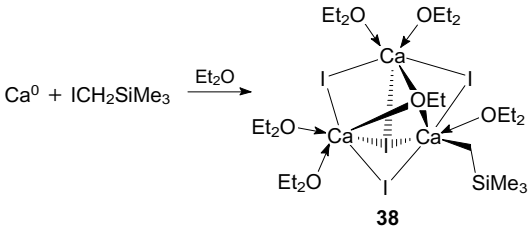
Table 2. Selected interatomic distances (Å) in alkyl halide complexes $RMX(Solv)_n$.

Complex	M – C	M – Hal	M – O	M···X	Ref.
$\{[(Me_3Si)_3C]Yb(\mu\text{-}I)(OEt_2)\}_2$ (**28**)	2.47(2)	3.084(2)	2.348(13)	–	68
		3.087(2)			
$\{[(Me_3Si)_2C(SiMe_2CH{=}CH_2)]Yb(\mu\text{-}I)(OEt_2)\}_2$ (**29**)	2.50(2)	3.076(2)	2.37(2)	Yb···(CH=CH$_2$)	69
		3.114(2)		2.98(2)	
$\{[(Me_3Si)_2C(SiMe_2OMe)]Yb(\mu\text{-}I)(OEt_2)\}_2$ (**30**)	2.580(2)	3.099(2)	2.35(2)	Yb – OMe	69
		3.116(2)		2.38(2)	
$(Me_3SiCH_2)CaBr(THP)_4$ (**34**)	2.500(2)	2.898(2)	2.369(2)-2.413(2)	–	52
$(Me_3SiCH_2)CaI(THP)_4$ (**35**)	2.528(2)	3.191(2)	2.389(2) – 2.411(2)	–	70
$[(Me_3SiCH_2)Ca(THF)_3(\mu\text{-}Cl)]_2$ (**37**)	2.527(2)	2.736(2)	2.390(2) – 2.426(2)	–	52
		2.788(2)			
$[(Pr^i_3SiCH_2)Ca(THF)_3(\mu\text{-}Br)]_2$ (**36**)	2.508(2)	2.897(2)	2.375(2) – 2.447(2)	–	52
				2.512(2)	

Scheme 11



Scheme 12



presence of LiCl. An alternative approach includes the reaction of PhCaI with KCH_2SiMe_3 and LiCl in THF.

The structures of complexes **34** – **37** were confirmed by X-ray diffraction study to establish that complexes **34** and **35** were monomers, whereas **36** and **37** were dimers, in which two metal centres were bridged by two halide anions (see Table 2).

By the example of iodide complex **35** it was shown that CH_2SiMe_3 moiety is fairly labile and is readily involved in the transalkylation with various aryl iodides R – I (R = Ph, C_6F_5, $C_6H_2Me_3$-2,4,6, C_6H_4I), and also with triphenyliodoethylene $IC(Ph){=}CPh_2$ and cyclopropyl iodide, but no products of the Wurtz reaction containing the C – C bond were detected.[71]

When Et_2O serves as a solvent (in place of THF), the reaction of Ca metal with ICH_2SiMe_3 proceeds with the cleavage of the C – O bond of the solvent.[71] One of the products, which was isolated and structurally characterized, proved to be a trinuclear calcium complex **38** (Scheme 12). In compound **38**, three metal centres are interconnected by four bridging iodide ligands and one μ^3-bridging ethoxide moiety. Here, a covalently bonded CH_2SiMe_3 group {Ca – C [2.452(3)] Å} is present in the coordination sphere of one of the calcium atoms.

3.2. Bis(alkyl) complexes

Bis(alkyl) derivatives of divalent lanthanides and heavy alkaline earth metals containing silyl-substituted alkyl ligands were obtained by exchange reaction of iodides MI_2 (M = Ca, Sr, Ba, Yb, Sm, Eu) with the corresponding alkylpotassium reagents KR.

An exchange reaction of MI_2 with $K[C(SiMe_3)_3]$ in aromatic solvents affords the corresponding bis(alkyl) derivatives $M[C(SiMe_3)_3]_2$ **39** – **42** (Scheme 13). The use of bulky tris(trimethylsilyl)-substituted methyl ligand results in the absence of coordinated Lewis bases in complexes **39** – **42**. According to X-ray diffraction data, the metal atoms are covalently bonded to two carbon atoms of alkyl groups (Table 3). In this case, short contacts between metal ions and methyl carbons were detected.

Coordinative unsaturation of complexes **39** – **42** accounts for their extremely high reactivity. Thus, the treatment of complex Yb(II) **40** with diethyl ether[74] or carrying out an exchange reaction of YbI_2 with $K[C(SiMe_3)_3]$ in Et_2O (see Ref. 75) result in the cleavage of the C – O bond of the solvent, elimination of alkane $HC(SiMe_3)_3$ and ethylene, and affords a heteroleptic alkyl-alkoxide derivative **43** (Scheme 14). The reaction of calcium

Scheme 13

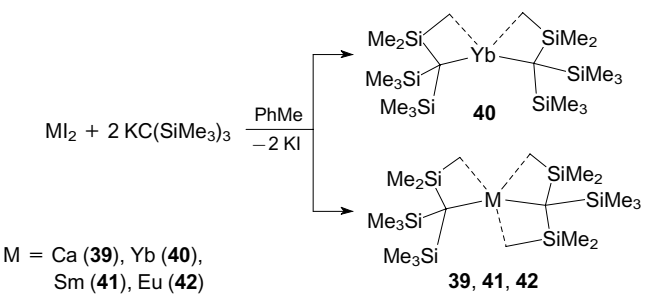
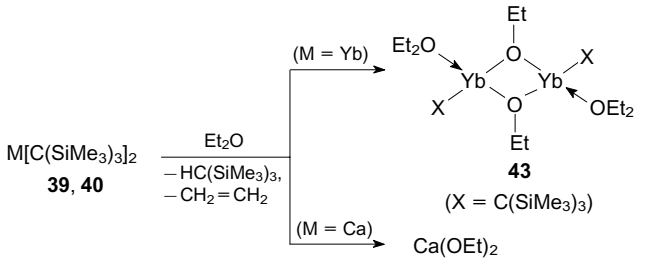


Table 3. Selected interatomic distances (Å) and bond angles (deg.) in bis(alkyl) complexes $M[C(SiMe_3)_3]_2$.

Complex	M – C	∠C – M – C	M···Me	∠M – C – Si	Ref.
$Ca[C(SiMe_3)_3]_2$ (**39**)	2.459(9)	149.7(5)	2.794(9) – 3.118(9)	89.0(6) – 98.4(7)	7
				106.6(7) – 118.5(7)	2
$Yb[C(SiMe_3)_3]_2$ (**40**)	2.490(4)	137.0(4)	2.852(5)	89.6(3) – 96.6(3)	68
	2.501(4)		2.900(5)	125.7(3) – 125.8(3)	
$\{[(Me_3Si)_3C]Yb(\mu\text{-}OEt)(OEt_2)\}_2$ (**43**)	2.574(4)	–	–	–	74
$Sm[C(SiMe_3)_3]_2$ (**41**)	2.584(4)	143.4(2)	2.984(4) – 3.210(5)	89.5(4) – 96.2(4)	73
	2.588(4)			108.9(4) – 118.0(4)	
$Eu[C(SiMe_3)_3]_2$ (**42**)	2.605(6)	136.0(4)	2.947(8) – 3.185(9)	87.8(6) – 94.7(5)	69
	2.612(7)			110.7(6) – 118.0(6)	

Scheme 14



analogue **39** with Et_2O immediately yields calcium ethoxide $Ca(OEt_2)_2$.[72]

The use of less bulky disilyl-$[(Me_3Si)_2CH]$ or trisilyl-substituted $[(Me_2SiH)_3C]$ groups enables the synthesis of bis(alkyl) complexes, which are more stable towards ethereal solvents.

It was shown that in the case of $[(Me_3Si)_2CH]^-$ ligand, the composition and structure of alkyl derivatives of Yb(II) and heavy alkaline earth metals formed in exchange reactions between MI_2 and $K[CH(SiMe_3)_2]$, depend on the solvent nature. Thus, the reaction in solvating solvents (THF, Et_2O) gives rise to bis(alkyl) complexes as adducts with Lewis bases $[(Me_3Si)_2CH]_2M(Solv)_n$ **44** – **46**[76] (Scheme 15, Table 4).

Similar reactions in benzene furnish ate-complexes $\{(Me_3Si)_2CH]_3M\}\{K\}$ **48** – **49**, which are solvent-separated ion pairs.[74, 75, 77] Frankland and Lappert[78] reported that the treatment of *para*-toluenesulfonates $M(SO_2C_6H_4Me\text{-}4)_2$ of

Scheme 15

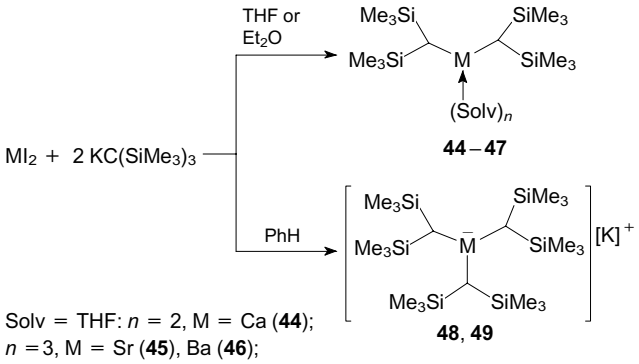


Table 4. Selected interatomic distances (Å) and bond angles (deg.) in bis(alkyl) complexes $[(Me_3Si)_2CH]_2M(Solv)_n$, $[(Me_2SiH)_3C]_2M(Solv)_n$, and $[Me_3SiCH_2]_2M(Solv)_n$.

Complex	M – C	∠C – M – C	M···Si	M···H	Ref.
$[(Me_3Si)_2CH]_2Ca(THF)_2$ (**44**)	2.493(2)	135.5(1)	–	–	76
$[(Me_3Si)_2CH]_2Ca(diox)_2$ (**53**)	2.483(3)	133.7(3)	–	–	79
$[(Me_3Si)_2CH]_2Ca(OPPh_3)_2$ (**54**)	2.540(2)	111.7(3)	–	–	80
$[(Me_3Si)_2CH]_2Ca(NHC)_2$ (**55**)	2.484(5)	110.3(5)	–	α-H(C) 2.85(5)	81
	2.528(5)			2.81(5)	
$[(Me_3Si)_2CH]_2Sr(THF)_3$ (**45**)	2.681(3)	126.3(2)	–	–	76
	2.692(3)				
$[(Me_3Si)_2CH]_2Ba(THF)_3$ (**46**)	2.827(3)	124.5(2)	–	–	76
	2.879(3)				
$[(Me_2SiH)_3C]_2Ca(THF)_2$ (**56**)	2.615(3)	132.9(3)	3.216(3)	β-H(Si) 2.53(3)	82
$[(Me_2SiH)_3C]_2Yb(THF)_2$ (**57**)	2.596(4)	131.5(4)	3.190(3)	β-H(Si) 2.49(3)	82
$[(Me_2SiH)_3C]_2Yb(TMEDA)$ (**60**)	2.675(4)	121.8(4)	3.142(4)	β-H(Si) 2.35(4)	83
	2.684(4)		3.191(4)	2.48(5)	
$[(Me_2SiH)_3C]_2Sm(THF)_2$ (**58**)	2.733(4)	134.0(4)	3.303(4)	β-H(Si) 2.64(4)	84
$[(Me_2SiH)_3C]_2Yb(NHC)$ (**61**)	2.610(3)	138.7(4)	3.118(1)	β-H(Si) 2.42(4)	84
	2.626(3)			2.50(4)	
$[(Me_2SiH)_3C]_2Sm(NHC)$ (**62**)	2.739(2)	131.7(2)	3.269(2)	β-H(Si) 2.53(3)	84
	2.779(2)		3.292(2)	2.65(3)	
$(Me_3SiCH_2)_2Ca(THP)_4$ (**71**)	2.561(3)	178.9(2)	–	–	71
	2.570(3)				
$(Me_3SiCH_2)_2Ca(TMEDA)_2$ (**72**)	2.583(4)	176.9(2)	–	–	71
	2.604(4)				

heavy alkaline earth metals with two equivalents of $K[CH(SiMe_3)_2]$ in THF also led to ate-complexes of the general formula $KM[CH(SiMe_3)_2]_3(THF)_3$ [M = Ca (**50**), Sr (**51**), Ba (**52**)], which were characterized by spectral methods.

Using calcium complex $[(Me_3Si)_2CH]_2Ca(THF)_2$ (**44**) as an example, it was demonstrated that THF molecules in the coordination sphere of the metal could be replaced with dioxane, triphenylphosphine oxide [$Ph_3P(O)$] or NHC-carbene (NHC is 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene) to give the corresponding adducts $[(Me_3Si)_2CH]_2Ca(Solv)_n$ [Solv = 1,4-dioxane (diox) (**53**),[79] Ph_3PO (**54**),[80] NHC (**55**)][81] (Scheme 16, see Table 4).

To synthesize bis(alkyl) complexes of heavy alkaline earth metals and divalent lanthanides, Sadow and co-workers[82–84] used alkyl ligand $[C(SiHMe_2)_3]^-$, containing three $SiHMe_2$ substituents at the methanide carbon atom. It was shown that the corresponding bis(alkyl) derivatives could be obtained as adducts with THF (**56**–**58**), or with TMEDA (**59**, **60**) (Scheme 17). Coordinated THF molecules in complexes **57** and **58** can be easily replaced with heterocyclic NHC-carbene ligand to afford complexes $[(Me_2SiH)_3C]_2Ln(NHC)$ **61**, **62**, (NHC is 1,3-di-*tert*-butylimidazol-2-ylidene).

In all complexes, agostic interactions between metal ions and Si–H bonds of the alkyl ligands were detected. In complexes **56**–**58**, **60**, and **62**, M···SiH agostic interactions are realized only for one of the $SiHMe_2$ groups of each of the alkyl ligands, whereas in complex Yb(II) **61** one of the alkyl ligands demonstrates two agostic interactions at once (see Table 4).

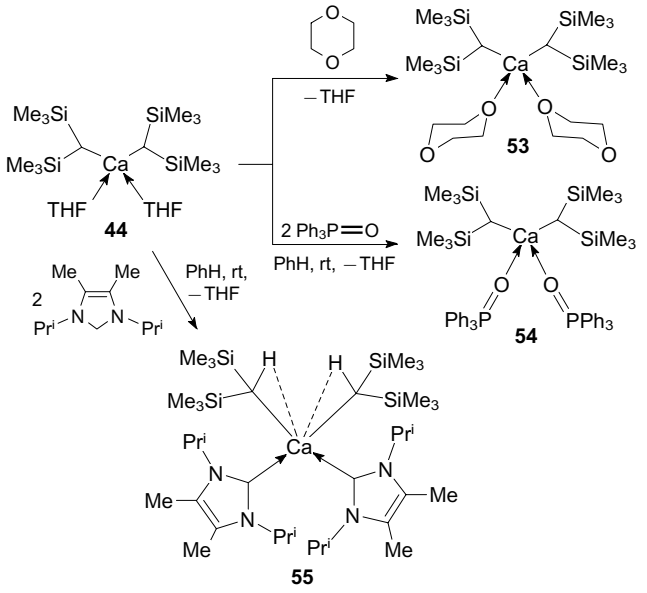
Bis(alkyl) derivatives **56** and **57** possess high thermal stability. No decomposition was observed even on heating the solutions of these compounds in benzene-d_6 at 60 °C for several days. However, an increase in temperature to 120 °C led to complete decomposition of the complexes in 120 and 96 h, respectively. The decomposition was accompanied by the elimination of the alkyl ligand $HC(SiHMe_2)_3$, probably due to the proton abstraction from THF molecules, with no signs of β-H(Si) hydride decomposition.

Sadow and co-workers[82–84] demonstrated that the abstraction of the H atom from the β-position of the $[(Me_2SiH)_3C]$ ligand occurs when bis(alkyl) complexes **56**–**60** are treated with Lewis acids $B(C_6F_5)_3$ or Me_3SiI. The reaction of complexes **55**–**60** with an equimolar amount of $B(C_6F_5)_3$ affords monoalkyl zwitterionic complexes **63**–**67**, containing triphenylhydroborate anion $[HB(C_6F_5)_3]^-$ (Scheme 18). This reaction is accompanied by the abstraction of β-hydride hydrogen from the silicon atom by the Lewis acid $B(C_6F_5)_3$ and elimination of silylene $Me_2Si{=}C(SiHMe_2)_2$, which is dimerized into 1,3-disilacyclobutane $[Me_2Si-C(SiHMe_2)_2]_2$. The structures of complexes of Ca **63** and Yb(II) **64** were confirmed by X-ray diffraction analysis.

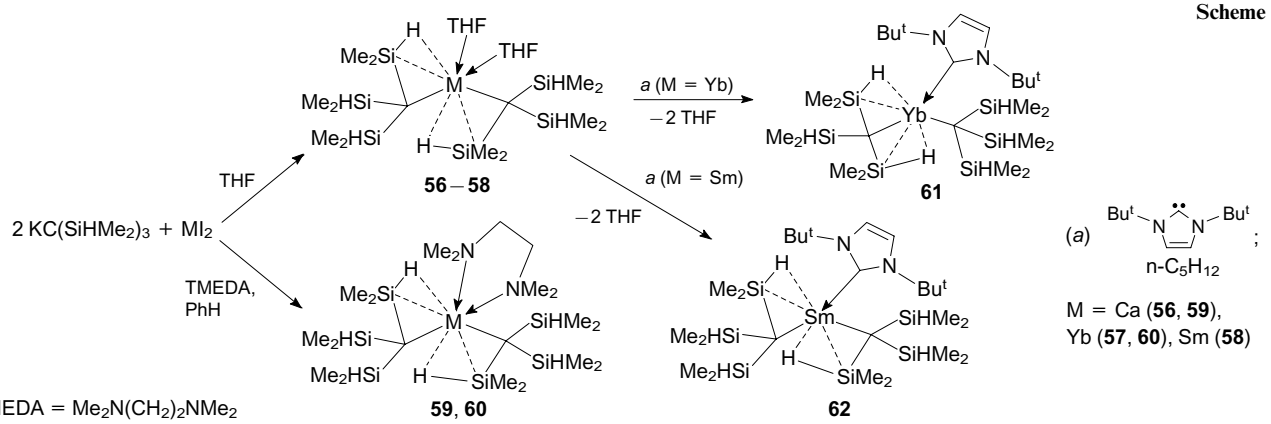
The reaction of complexes **56**–**60** with two equivalents of $B(C_6F_5)_3$ proceeds with the abstraction of two alkyl ligands and gives quantitatively $[Me_2Si-C(SiHMe_2)_2]_2$ and bis(triphenylhydroborate) derivatives **68**–**70** (see Scheme 18).

Bis(alkyl) complexes of Ca **56** and Yb(II) **57** react with an equimolar amount of Me_3SiI, like with $B(C_6F_5)_3$, to abstract the β-hydrogen atom furnishing a mixture of Me_3SiH and 1,3-disilacyclobutane (Scheme 19). The authors suggest that the reaction of bis(alkyl) derivatives **56** and **57** with Me_3SiI affords unstable alkyl iodide derivatives $[(Me_2SiH)_3C]MI(THF)_n$, which undergo symmetrization yielding $MI_2(THF)_2$ and the starting complexes **56** and **57**. The reaction of TMEDA-containing complexes **59** and **60** with Me_3SiI proceeds in a different way. The major product is $Me_3SiC(SiHMe_2)_3$, formed *via* metathesis of the M–C and Si–I σ-bonds. In this case, the products of the β-hydrogen elimination from $SiHMe_2$ groups of the ligand ($HSiMe_3$ and 1,3-disilacyclobutane) were detected in moderate amounts (up to 25%). The authors' explanation is that in the case of adducts with TMEDA, the less steric crowd-

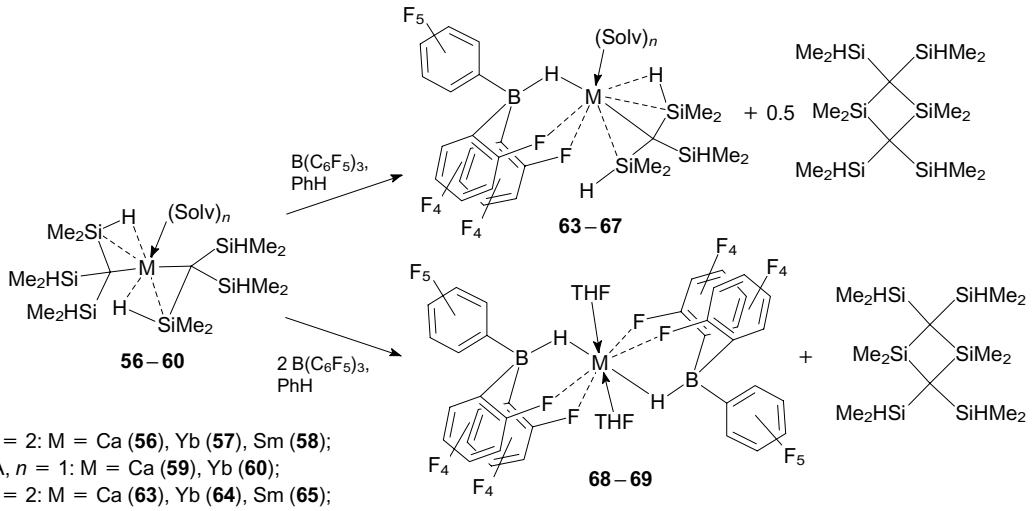
Scheme 16



Scheme 17

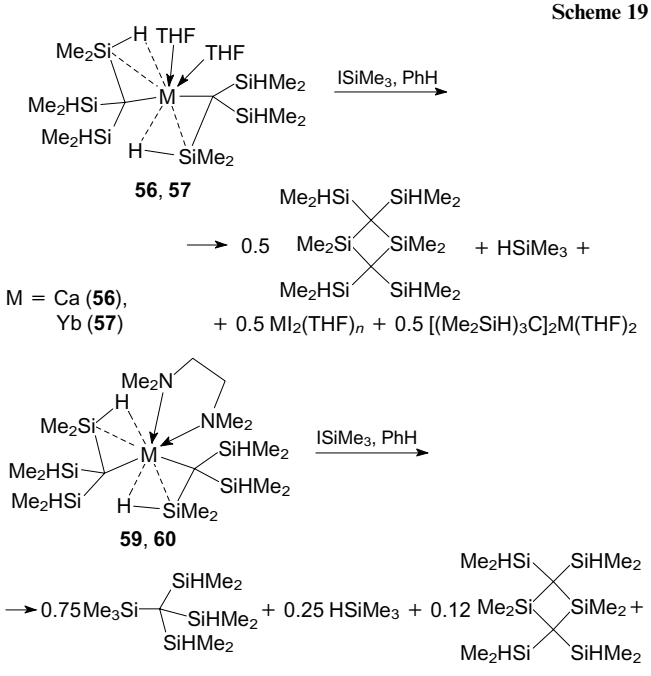


Scheme 18



Solv = THF, *n* = 2: M = Ca (**56**), Yb (**57**), Sm (**58**);
Solv = TMEDA, *n* = 1: M = Ca (**59**), Yb (**60**);
Solv = THF, *n* = 2: M = Ca (**63**), Yb (**64**), Sm (**65**);
Solv = TMEDA, *n* = 1: M = Ca (**66**), Yb (**67**);
M = Ca (**68**), Yb (**69**), Sm (**70**)

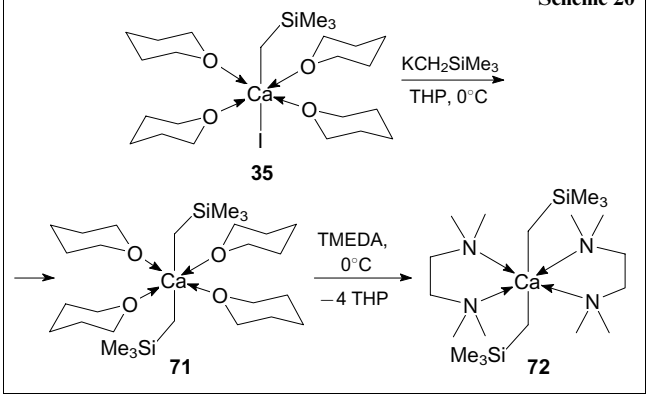
Scheme 19



M = Ca (**56**), Yb (**57**)

M = Ca (**59**), Yb (**60**)

Scheme 20



ing around the metal coordination sphere makes the M – C bond more accessible to the attack by Me_3SiI, and promotes the metathesis of σ-bonds, rather than the H-atom abstraction from the ligand.

For a long time, one failed to synthesize bis(alkyl)calcium complexes containing monosilyl-substituted alkyl ligand CH_2SiMe_3 because of the side Wurtz reactions occurring during the reaction of CaI_2 and KCH_2SiMe_3, and also the cleavage of ethers at the α-position. In 2017, Koch *et al.*[71] succeeded to obtain and structurally characterize calcium complex **71** *via* the reaction of KCH_2SiMe_3 with $(Me_3SiCH_2)CaI(THP)_4$ (**35**) (Scheme 20, see Table 4). The treatment of **71** with TMEDA leads to displacement of the THP molecules to afford $(Me_3SiCH_2)_2Ca(TMEDA)_2$ (**72**).

Silyl-substituted alkyl ligands containing Lewis bases at the silicon atoms were also successfully used in the synthesis of bis(alkyl) derivatives of Ln(II) and heavy alkaline earth metals. In 1996, Eaborn *et al.*[69] obtained a series of low-coordinated bis(alkyl) derivatives of ytterbium **73** – **75**, in which one of the silicon atoms was substituted with OMe, CH_2CH_2OEt, $CH{=}CH_2$ (Scheme 21). As a synthetic strategy, an exchange reaction between YbI_2 and the corresponding potassium derivatives $K[C(SiMe_3)_2(SiMe_2R)]_2$ in benzene was employed. Also, it was shown that the bis(alkyl) derivatives can be obtained *via* thermolysis of alkylytterbium(II) iodide complexes **29** and **30** in high vacuum. The thermolysis was accompanied by sublimation of bis(alkyl) derivatives $Yb[C(SiMe_3)_2(SiMe_2R)]_2$ (see Scheme 21).

The exchange reactions between MI_2 (M = Sm, Sr, Ba) and $[(Me_3Si)_2(MeOMe_2Si)C]K$ in THF produced the solvated complexes **76**,[85] **77**, **78**[86] (Scheme 22, Table 5).

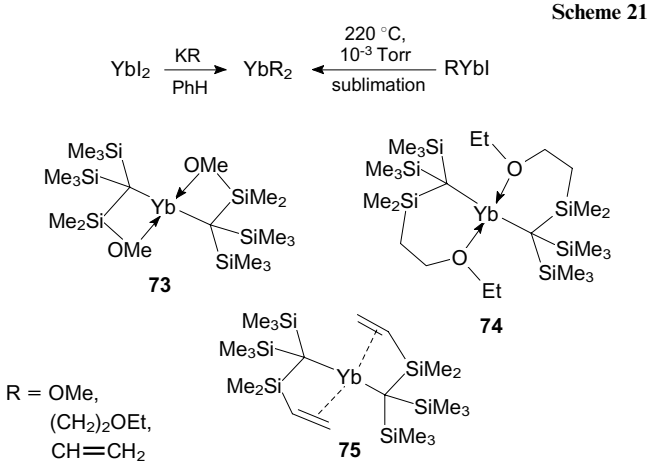
The synthesis of complex $Ca[C(SiMe_3)_2(SiMe_2hpp)]_2$ (**79**) {hppH is 1,3,4,6,7,8-hexahydro-2*H*-pyrimido[1,2-a]-pyrimidine}, substituted with tris(silyl)-substituted alkyl ligands with a bicyclic guanidinate donor moiety at one of the silicon atoms, was reported (Scheme 23, see Table 5).[87]

Lanthanide(II) bis(alkyl) derivatives were also prepared using dianionic tris(silyl)-substituted alkyl ligands in which two methanide carbons were linked by bridges of various lengths and nature.[88] It was found that an exchange reaction between YbI_2 and potassium derivatives

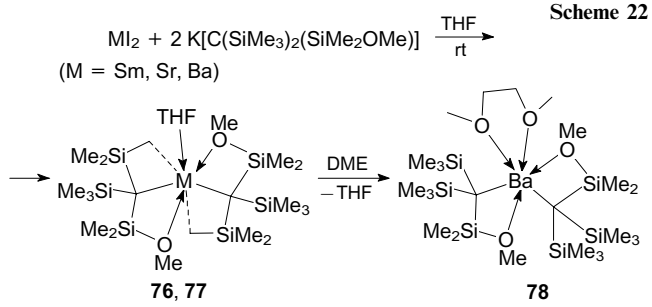
Table 5. Selected interatomic distances (Å) and bond angles (deg.) in bis(alkyl) complexes containing polydentate silyl-substituted alkyl ligads.

Complex	M – C	M – X	M···Me	∠C – M – C	Ref.
$[(Me_3Si)_2(MeOMe_2Si)C]_2Sm(THF)$ (**76**)	2.787(5)	2.520(3)	3.181(5)	144.7(2)	85
	2.845(5)	2.570(3)	3.383(5)		
$[(Me_3Si)_2(MeOMe_2Si)C]_2Sr(THF)$ (**77**)	2.786(3)	2.493(2)	3.200(3)	144.9(2)	86
	2.849(3)	2.543(2)	3.394(3)		
$[(Me_3Si)_2(MeOMe_2Si)C]_2Ba(DME)$ (**78**)	3.036(2)	2.677(2)	–	139.9(2)	86
	3.049(2)	2.709(2)			
$Ca[C(SiMe_3)_2(SiMe_2hpp)]_2$ (**79**)	2.664(2)	2.356(2)	3.039(3)	144.5(2)	87
	2.681(2)	2.382(2)			
$[(Me_3Si)_2C(SiMe_2))_2O]Yb(THF)_2$ (**80**)	2.713(2)	2.373(2)	–	130.7(1)	88
$[\{(Me_3Si)(Me_2MeOSi)CSiMe_2CH_2\}_2]Yb(THF)$ (**81**)	2.607(3)	2.405(3)	–	128.5(1)	88
	2.642(3)	2.421(2)			

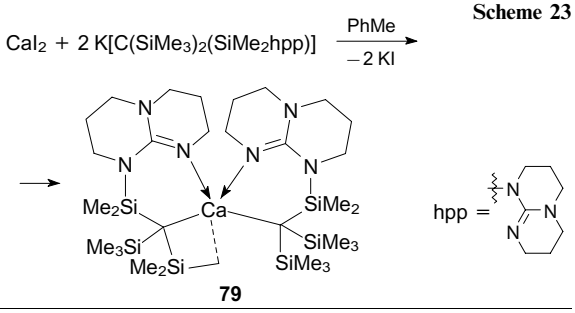
Scheme 21



Scheme 22

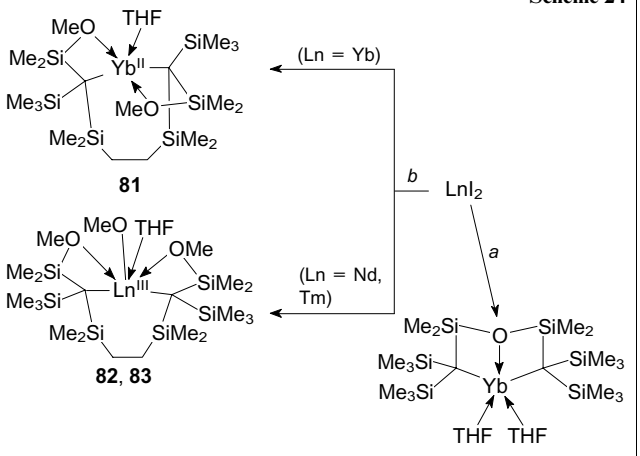


Scheme 23



$[\{(Me_3Si)_2CSiMe_2\}_2O]K_2(OEt_2)$ (L1) and $[\{(Me_3Si)(Me_2MeOSi)CSiMe_2CH_2\}_2]K_2$ (L2) proceeds to give the corresponding Yb(II) alkyl complexes **80** and **81**, containing *ansa*-bonded dicarbanionic ligands (Scheme 24, see Table 5).

Scheme 24



(*a*) $[\{(Me_3Si)_2CSiMe_2\}O]K_2(OEt_2)$, THF;
(*b*) $[\{(Me_3Si)(Me_2MeOSi)CSiMe_2CH_2\}_2]K_2$, THF;
Ln = Nd, Tm (product mixture), Yb (**80**, **81**), Nd (**82**), Tm (**83**)

Similar reactions of divalent Nd and Tm iodides failed to produce the corresponding bis-alkyl derivatives. When dipotassium complex of L1 reacted with NdI_2 and TmI_2, a mixture of unidentified products was obtained. At the same time, the exchange reactions of complex L2 with these iodides led to the oxidation of metal centres to the trivalent state and the formation of alkyl methoxide complexes **82** and **83** (see Scheme 24). The authors believe that methoxy ligands are formed due to the cleavage of the Si – O bond of the ligand.

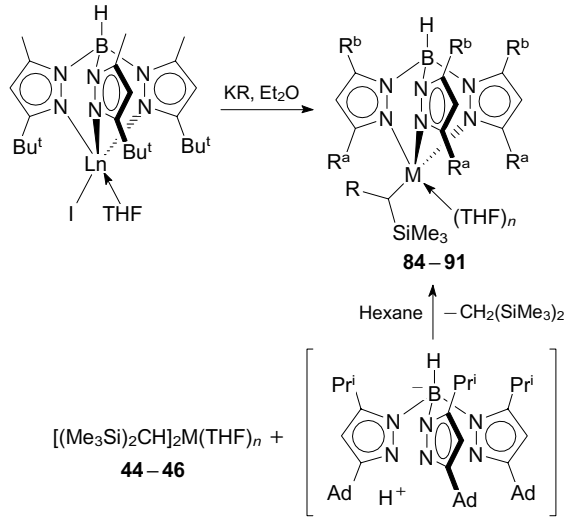
3.3. Heteroleptic alkyl complexes

For the synthesis of mixed-ligand complexes [L]MR, two synthetic approaches were used, the first including the exchange reactions between heteroleptic iodide derivatives [L]MI and equimolar amounts of RK. The second approach is based on the elimination of alkane RH resulting from protonolysis of the M – C bond of bis(alkyl) complexes R_2M under the action of pro-ligands [L]H.

The first heteroleptic Ln(II) derivatives containing silyl-substituted ligands were Yb(II) monoalkyl complexes **84** and **85**, which were obtained by Takats and co-workers [89] in 1994 *via* exchange reactions of iodide $[Tp^{Bu^t,Me}]YbI(THF)$ with equimolar amounts of KR (Scheme 25, Table 6). Later, the same authors obtained analogues for Sm(II) **86**, **87**,[90] and even for Tm(II) **88**,[98] the +2 oxidation state of which in extremely unstable. It was noted that the reactions of $[Tp^{Bu^t,Me}]SmI(THF)$ and KCH_2SiMe_3 proceed with the

redistribution of Tp ligands and alkyl groups to afford a homoleptic complex $[Tp^{Bu^t,Me}]_2Sm$ and presumably an unstable bis(alkyl) derivative $[Sm(CH_2SiMe_3)_2]$.[90] Heteroleptic analogues of alkaline earth metals **89** – **91** (see Scheme 25, Table 6), containing tris(triazolyl)borate ligands bearing bulky adamantyl substituents, were obtained by the alkane elimination in the reaction of the corresponding bis(alkyl) complexes $[(Me_3Si)_2CH]_2M(THF)_n$ (**44** – **46**) with $[Tp^{Ad,Pr^i}]H$.[91]

Scheme 25



R^a = Bu^t, R^b = Me: R = H, M = Yb, *n* = 1 (**84**);
R = $SiMe_3$: M = Yb, *n* = 0 (**85**), Sm, *n* = 0 (**86**), Sm, *n* = 1 (**87**), Tm, *n* = 0 (**88**);
R^a = Ad, R^b = Pr^i: R = $SiMe_3$, *n* = 0: M = Ca (**89**), Sr, (**90**), Ba (**91**)

Takats and co-workers[99] investigated the reaction of complex **84** with an excess of tetramethylimidazol-2-ylidene. It turned out that the reaction leads not only to the replacement of the THF molecule with carbene but also to alkyl group elimination due to the activation of the $C_{sp3}-H$ bond of one of the N – Me groups in the NHC-carbene ligands. The reaction product was a novel Yb(II) alkyl complex **92** (Scheme 26).

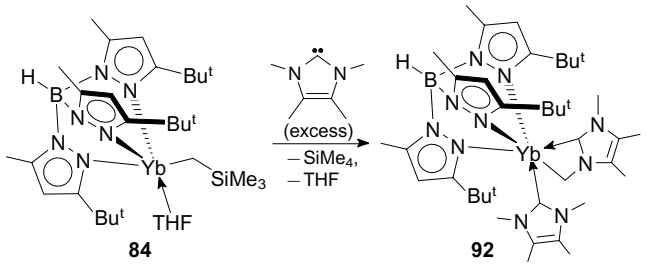
Heteroleptic alkyl complexes of Yb(II) **84** and Ba **91**, containing tridentate tris(pyrazolyl)borate ligands, were shown to be convenient reagents for the synthesis of corresponding hydrides *via* hydrogenolysis of the M – C σ-bond.[89, 100] The treatment of complexes **84** and **91** with molecular H_2 at a pressure of 120 and 20 atm produces dimeric hydrides **93**, **94**, respectively, in which two metal centres are bridged by two hydride ligands (Scheme 27).

It was found that the stability of a series of heteroleptic alkyl complexes of alkaline earth metals (Ca, Sr, Ba) and Yb(II) that contain β-diketoiminate ligands depends on the ionic radius of a metal.[92, 101] For Ca and Yb(II) ions, characterized by the smallest radii, the reaction of bis(alkyl) derivatives $[(Me_3Si)_2CH]_2Ca(THF)_2$ with β-diketoimine [BDI]H [$(Pr^i_2C_6H_3)N{=}C(Me)CHC(Me)$-$NH(C_6H_3Pr^i_2)$], or exchange reaction between $\{[BDI]Yb(\mu\text{-}I)(THF)\}_2$ and

Table 6. Selected interatomic distances (Å) and bond angles (deg.) in heteroleptic complexes $[L]M[R](Solv)_n$.

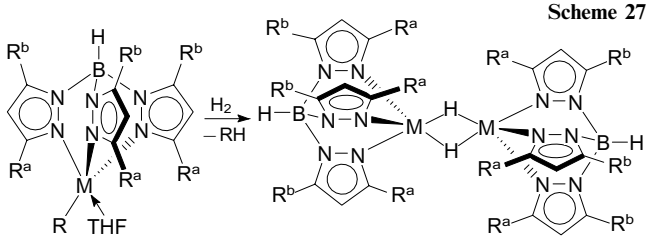
Complex	M – C	M···Me	M···H(Cα)	∠M – C – Si	Ref.
$[Tp^{Bu^t,Me}]Yb[CH_2SiMe_3](THF)$ (**84**)	2.526(4)	–	2.91(5)	135.8(4)	89
$[Tp^{Bu^t,Me}]Yb[CH(SiMe_3)_2]$ (**85**)	2.554(5)	3.085(4)	–	98.4(5)	89
				132.1(5)	
$[Tp^{Bu^t,Me}]Sm[CH(SiMe_3)_2]$ (**86**)	2.667(5)	3.137(6)	3.02(5)	100.0(4)	90
				129.9(4)	
$[Tp^{Bu^t,Me}]Sm[CH(SiMe_3)_2](THF)$ (**87**)	2.697(4)	3.276(6)	3.06(5)	102.5(3)	90
				125.7(3)	
$[Tp^{Bu^t,Me}]Tm[CH(SiMe_3)_2]$ (**88**)	2.554(3)	3.123(4)	2.90(5)	100.8(3)	81
				132.2(2)	
$[Tp^{Ad,Pr^i}]Ca[CH(SiMe_3)_2]$ (**89**)	2.440(1)	3.307(1)	2.76(2)	108.6(2)	91
				127.8(2)	
$[Tp^{Ad,Pr^i}]Sr[CH(SiMe_3)_2](THF)$ (**90**)	2.620(7)	3.219(8)	2.94(8)	103.9(7)	91
				126.9(7)	
$[BDI]Yb[CH(SiMe_3)_2](THF)$ (**96**)	2.562(8)	–	2.98(6)	110.2(6)	92
	2.549(7)				
$[N^-,N]Sr[CH(SiMe_3)_2](THF)_2$ (**100**)	2.706(4)	–	–	112.1(3)	93
				120.9(3)	
$[N^-,N]Ba[CH(SiMe_3)_2](THF)_2$ (**101**)	2.834(8)	–	–	112.5(6)	93
	2.840(7)			120.8(5)	
$[BDI^{N,N}]Yb[CH_2SiMe_3]$ (**102**)	2.499(5)	–	–	118.1(4)	94
$[BDI^{N,N}]Sm[CH(SiMe_3)_2]$ (**103**)	2.707(5)	–	–	113.4(4)	95
				115.6(4)	
$[LO^{NO_2}]Ca[CH(SiMe_3)_2](THF)$ (**104**)	2.570(4)	–	2.92(5)	110.1(3)	96
				120.4(3)	
$[Cp^{Ar}]Ca[CH(SiMe_3)_2](THF)$ (**112**)	2.433(5)	–	2.83(5)	109.0(4)	97
				110.6(4)	
$[Cp^{Ar}]Sr[CH(SiMe_3)_2](THF)$ (**113**)	2.668(5)	–	3.02(5)	111.1(5)	97
				119.0(5)	
$[Cp^{Ar}]Ba[CH(SiMe_3)_2](THF)_2$ (**114**)	2.811(4)	–	3.17(5)	112.1(5)	97
				112.2(5)	
$[(Me_3Si)_2N]Ca[CH_2SiMe_3](PMDETA)_3$ (**119**)	2.532(2)	–	–	142.2(1)	52

Scheme 26



84 **92**

Scheme 27



84, **91** **93**, **94**

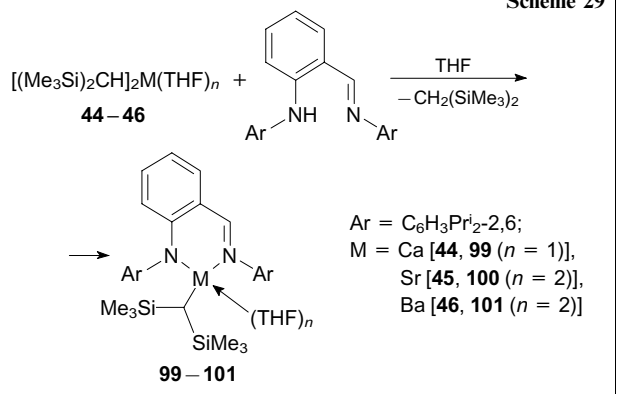
93: M = Yb, R^a = Bu^t, R^b = Me; **94**: M = Ba, R^a = Ad, R^b = Pr^i

$K[CH(SiMe_3)_2]$ (1 : 2 molar ratio) provides stable monoalkyl complexes of Ca (compound **95**)[101] and Yb (compound **96**)[92] (Scheme 28, see Table 6). For metals with larger ionic radii (Sr, Ba), the reaction of $[(Me_3Si)_2CH]_2M(THF)_2$ with [BDI]H under the similar conditions proceeds with deprotonation of the NH group of β-diketoiminate ligand and activation of one of the CH-bonds of the methyl group at the imine carbon, and furnish dimeric amino-methylene complexes of Sr (**97**) and Ba (**98**), containing the azapentadienide(azaallylic) dianion (see Scheme 28).[101]

The use in the alkane eliminations of anilido-imine ligand, which has the coordination site geometry similar to that of β-diketoiminate ligand, opened access to stable monoalkyl complexes including those for metals with large ionic radii (Sr and Ba).[93] Bis(alkyl) complexes $[(Me_3Si)_2CH]_2M(THF)_n$ **42**–**44** react with imino-substituted aniline with the elimination of one of the alkyl groups and afford the corresponding species **99**–**101** (Scheme 29). The structures of alkyl complexes of Yb(II) (**96**), Sr (**100**), and Ba (**101**), containing bidentate *N*,*N*-chelate β-diketoiminate and anilidoimine ligands, were confirmed by X-ray diffraction analysis (see Table 6).

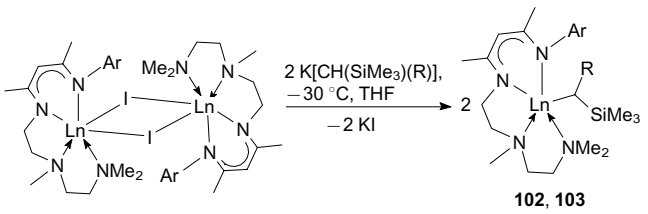
The use of a tetradentate β-diketoiminate ligand $[BDI^{N,N}]$ [$BDI^{N,N}$ = 2,6-Pr_2iC$_6$H$_3$NC(Me)CHC.(Me)N(CH$_2$)$_2$N(Me)(CH$_2$)$_2$NMe$_2$], substituted with donor (CH$_2$)$_2$N(Me)(CH$_2$)$_2$NMe$_2$ group at one of the nitrogen atoms of diketoiminate moiety, also provides heteroleptic

Scheme 29



alkyl complexes of Ln(II). The exchange reactions between dimeric iodide complexes $\{[BDI^{N,N}]M(\mu\text{-}I)\}_2$ (M = Yb, Sm) and two equivalents of K[CH(R)SiMe$_3$] (R = H, SiMe$_3$) yield heteroleptic monoalkyl derivatives of Yb (compound **102**)[94] and Sm (compound **103**)[95] (Scheme 30). Due to the use of tetradentate β-diketoiminate ligand, the newly formed complexes **102** and **103** contain no coordinated THF molecules. The M – C bond lengths in complexes **102** and **103** are 2.499(5) and 2.707(5) Å, respectively (see Table 6).

Scheme 30



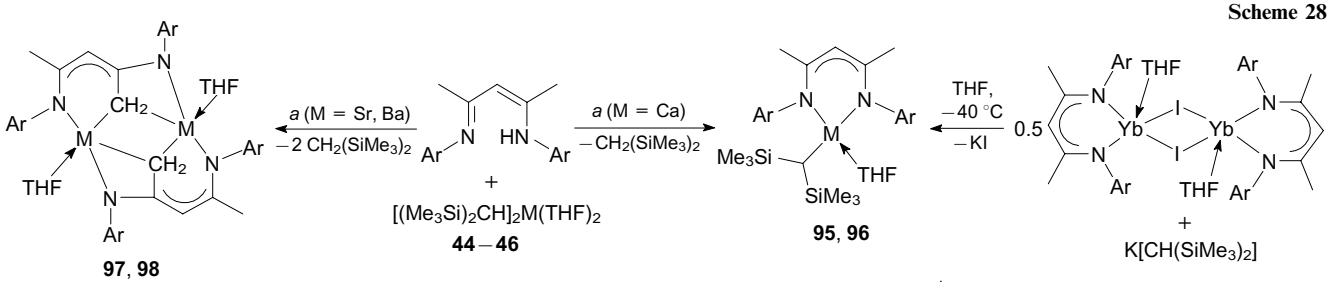
102, **103**

Ar = C$_6$H$_3$Pr$^i_2$-2,6; R = H, Ln = Yb (**102**); R = SiMe$_3$, Ln = Sm (**103**)

Examples of heteroleptic alkyl complexes of Ca and Sr containing a tetradentate phenoxide ligand [LO^{NO_2}] with a donor CH$_2$N(CH$_2$CH$_2$OMe)$_2$ group in the *ortho*-position was also reported. It was shown that when bis(alkyl) complexes **44** and **45** are treated with equimolar amounts of phenol [LO^{NO_2}]H, one alkyl group is eliminated to give derivatives $[LO^{NO_2}]M[CH(SiMe_3)_2](THF)_n$ **104**, **105** (Scheme 31, see Table 6).[96]

Reactions of bis(imino)acenaphthene (dipp-BIAN) and bis(imino)pyridine [2,6-(2,6-$Pr^i_2C_6H_3N{=}C(Me))_2$-NC_5H_3)] with bis(alkyl) complexes $[(Me_3Si)_2CH]_2M(THF)_n$ **44**–**46** proceed with the loss of aromaticity of acenaphthenic moieties of the ligands.[102, 103]

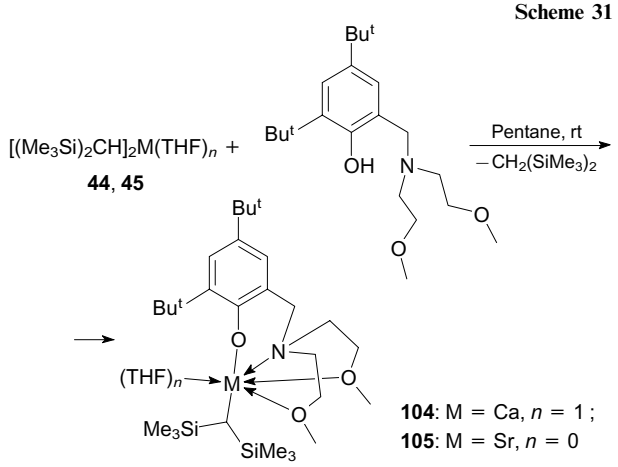
Scheme 28



97, **98** **95**, **96**

(*a*) Hexane, 60 °C; M = Ca (**95**), Yb (**96**), Sr (**97**), Ba (**98**); Ar = 2,6-$Pr^i_2C_6H_3$

Scheme 31



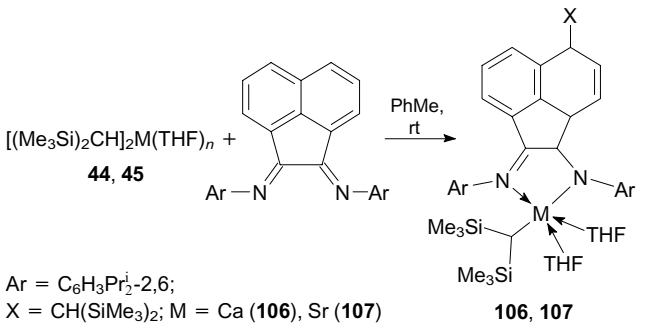
The reaction of dipp-BIAN with $[(Me_3Si)_2CH]_2M(THF)_n$ **44**, **45** gives stable monoalkyl derivatives $[(C^5\text{-}CH(SiMe_3)_2)(dipp\text{-}BIAN)]M[CH(SiMe_3)_2].(THF)_2$ **106**, **107**,[102] coordinated *via* a monoanionic bidentate *N*,*N*-ligand, which contains $(Me_3Si)_2CH$ group in the 5-position of acenaphthene moiety (Scheme 32). One of the nitrogen atoms of the newly formed monoanionic ligand is covalently bonded to the alkaline earth metal ion, while the second one is linked by a coordinate bond.

The reaction of bis(imino)pyridine $[2,6\text{-}(2,6\text{-}Pr^i_2C_6H_3N{=}C(Me))_2NC_5H_3)]$ with complexes **44**–**46** is also accompanied with dearomatization of the pyridine ring and gives a mixture of monoalkyl complexes **108a**,**b**, resulting from 1,4-addition of the M–C bond across the system of the imine C=N and pyridine C=C multiple bonds (**108a**) or 1,4-addition of the M–C bond across the pyridine ring (**108b**) (Scheme 33).[103] In complexes **108a**,**b**, the ligands become monoanionic. In this case, the metal atom is covalently bonded to the 'ex-imine' nitrogen atom of the ligand in complex **108a**, and the nitrogen atom of the dearomatized pyridine ring in complex **108b**. As the authors believe, the formed monoalkyl intermediates **108a**,**b** are unstable in solution and decompose to eliminate the alkyl groups that remain bonded to the metal. This is accompanied by the elimination of $CH(SiMe_3)_2$ substituents of the pyridine moiety, resulting in the restoration of the aromatic structure, and intramolecular activation of the CH bonds of the imine methyl groups, and furnishes complexes $[2,6\text{-}\{(Dipp)NC{=}CH_2)\}_2C_5H_3N]M(THF)$ **110**, **111**, containing dianionic diamide ligands.

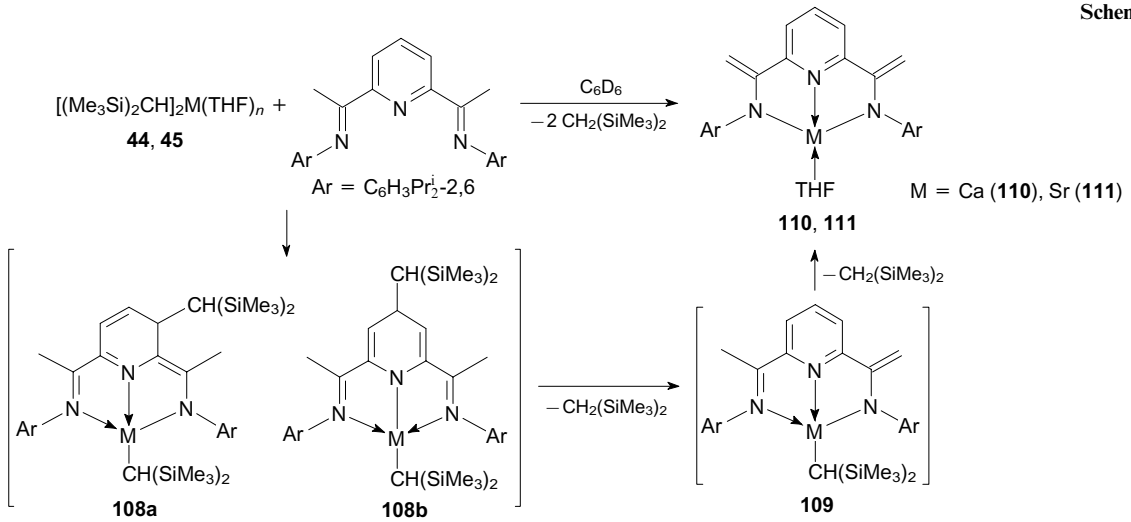
Despite the widespread use of cyclopentadienyl ligands in the chemistry of heavy alkaline earth metals, the synthesis of half-sandwich heteroleptic alkyl complexes was first reported only in 2019.[97] The reaction of an extremely bulky cyclopentadiene $[Cp^{Ar}]$ $[H(C_5(C_6H_3Pr^i_2\text{-}3,5)_5H]$ with bis(alkyl) complexes **44**–**46** readily proceeds in hexane at room temperature with the elimination of $CH_2(SiMe_3)_2$ to provide monoalkyl half-sandwich derivatives $[Cp^{Ar}]M[CH(SiMe_3)_2](THF)_n$ **112**, **113**, **114** (Scheme 34, see Table 6). Alkyl complexes **112**–**114** are convenient reagents for the synthesis of the corresponding hydride derivatives $\{[Cp^{Ar}]M(\mu\text{-}H)(Solv)\}_2$ (**115**–**117**) (see Scheme 34).

Koch *et al.*[52] reported that calcium complex $[(Me_3Si)_2N]Ca[CH_2SiMe_3](THF)_3$ (**118**), containing the silylamide moiety, can be obtained *via* the reaction of $(Me_3SiCH_2)CaI(THP)_4$ with $K[N(SiMe_3)_2]$ (Scheme 35). The treatment of **118** with tridentate *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (PMDETA) gives the corresponding adduct $[(Me_3Si)_2N]Ca[CH_2SiMe_3](PMDETA)$ (**119**) (see Table 6). Using complex **119** as an example, it was demonstrated that the Ca–C bonds are more reactive towards phenylsilane, and under the action of the latter, alkyl groups of $Ca\text{–}CH_2SiMe_3$ undergo the σ-bond metathesis. The reaction of compound **119** with $PhSiH_3$ yields a hexanuclear nonahydride cluster $\{[(Me_3Si)_2N]_3Ca_6(\mu\text{-}H)_9(PMDETA)_3\}$ (**120**), in which three

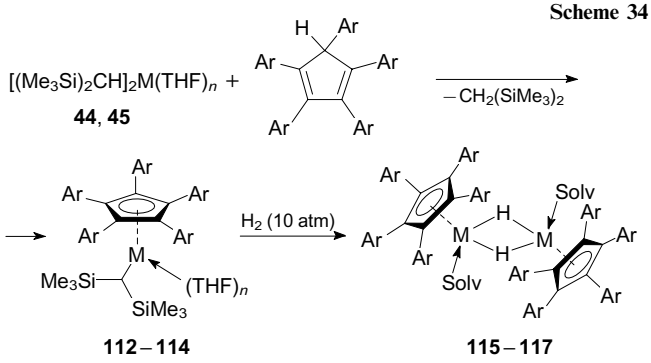
Scheme 32



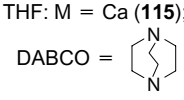
Scheme 33



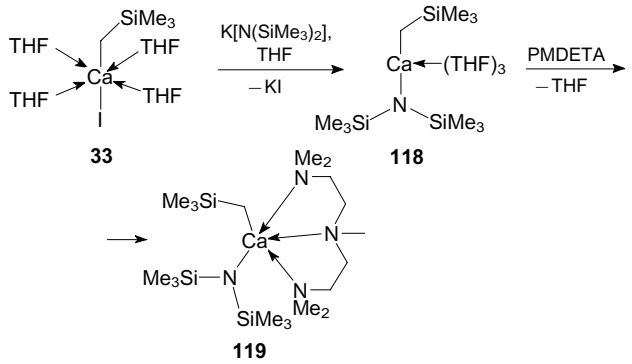
Scheme 34



Ar = $C_6H_3Pr^i_2$-3,5; M = Ca (**112**, *n* = 1), Sr (**113**, *n* = 2), Ba (**114**, *n* = 2); Solv = THF: M = Ca (**115**); Solv = DABCO: M = Sr (**116**), Ba (**117**);



Scheme 35



calcium atoms retain covalently bonded silylamide moieties. It should be emphasized that amido-hydride complex **120** had been previously obtained by the action of $PhSiH_3$ on bis(amide) calcium complex $[(Me_3Si)_2N]_2Ca$ in the presence of PMDETA.[104]

The reaction of bis(alkyl) complexes **44**, **45** with amine-borane adducts $R_2NH \cdot BH_3$ [R = Me, $(CH_2)_4$] was shown to proceed with the elimination of $CH_2(SiMe_3)_2$ and to afford heteroleptic alkyl complexes $\{[(Me_3Si)_2CH]M[R_2N(\mu\text{-}BH_3)]\}_2$ **121 – 124** (Scheme 36).[105, 106] In the crystalline state, complexes **121 – 124** are dimers in which two metal centres are bridged by borohydride groups. The authors note that these complexes are unstable and on heating in solution to 60 °C, they decompose to give alkylaminoborane $(Me_3Si)_2CHBHNR_2$ with the precipitation of MH_2.

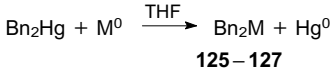
4. Complexes of Ln(II) and heavy alkaline earth metals containing α-arylalkyl ligands

The main advantage of α-arylalkyl ligands (benzyl, diphenylmethyl, triphenylmethyl) is the higher stability of their derivatives due to delocalization of the negative charge involving the aromatic ring. In this case, the absence of protons at β-carbon atoms, as in the case of α-silyl-substituted alkyl ligands, rule out the general possibility of β-hydride elimination. Moreover, the combination of bulky aryl-substituted methanide ligands with the possibility of non-bonded metal – arene interactions for them also provides kinetic and thermodynamic stabilization of metal complexes.

4.1. Benzyl complexes

The first reports on the synthesis of benzyl derivatives of heavy alkaline earth metals (Ca, Sr and Ba) appeared in 1978. Takahashi *et al.*[107] obtained a series of dibenzyl complexes $Bn_2M(THF)_n$ **125 – 127** *via* the reaction of Ca, Sr, and Ba metals with Bn_2Hg in THF (Scheme 37). Derivatives **125 – 127** were not isolated in the individual state but were characterized by NMR spectroscopy. Weeber *et al.*[108] described the synthesis of barium complex **127** in good yields (93 and 81%) by the exchange reactions of $[(Me_3Si)_2N]_2Ba(THF)_2$ and $[2,4,6\text{-}Bu^t_3C_6H_2O]_2Ba$, soluble in non-polar solvents, with two equivalents of BnLi(TMEDA). With dibenzylmagnesium Bn_2Mg(diox), the yield of complex **127** was as low as 40%.

Scheme 37



M = Ca (**125**), Sr (**126**), Ba (**127**)

The first pieces of evidence of the structure of dibenzyl derivatives of Ln(II) and heavy alkaline earth metals appeared much later. In 2004, Harder *et al.*[109] obtained calcium complexes **125** and **130** *via* exchange reactions of CaI_2 with $K[CH_2C_6H_4R\text{-}4]$ and characterized them (Scheme 38, Table 7).[109] Anwander and co-workers[110] have recently used complex $Bn_2Yb(THF)_n$ (**128**) to synthesize dibenzyl ytterbium complexes **129** and **131** (see

Scheme 36

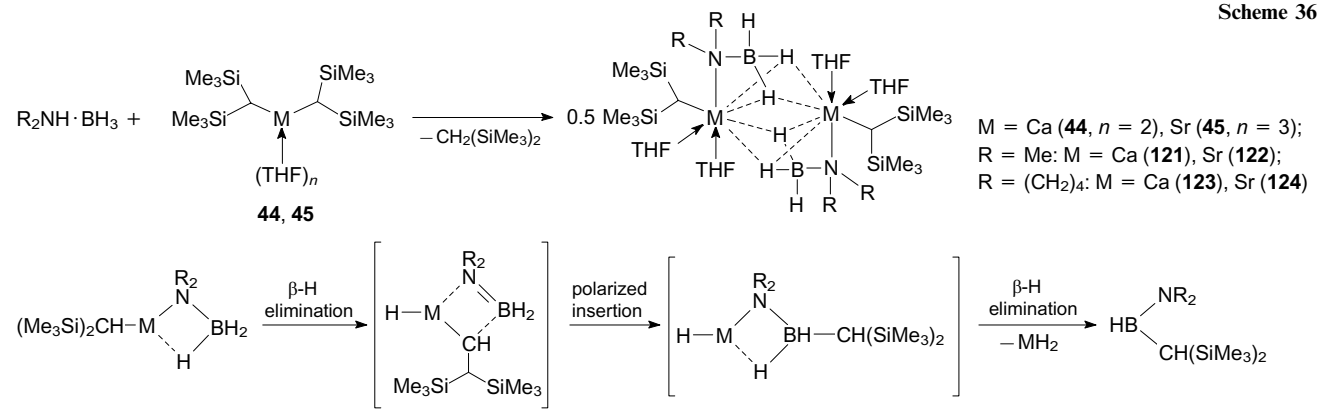
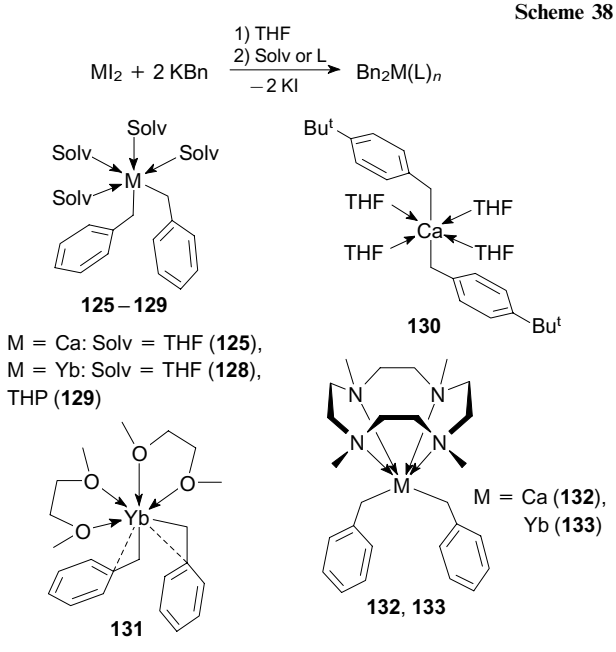


Table 7. Selected interatomic distances (Å) and bond angles (deg.) in dibenzyl complexes $[BnM(Solv)_m]_n$.

Complex	Coordination mode	M – C(α)	M···C (*ipso*)	M···C (*ortho*)	M···η⁶-C(Ar)	∠M – CH_2 – C (*ipso*)	∠C – M – C	Ref.
$Bn_2Ca(THF)_4$ (**125**)	κ¹-C	2.574(4)	3.502(4)	–	–	117.7(4)	90.9(4)	109
		2.595(4)	3.566(4)			120.7(4)		
$(4\text{-}Bu^tC_6H_4CH_2)_2Ca(THF)_4$ (**130**)	κ¹-C	2.592(4)	3.501(4)	–	–	118.1(4)	176.4(4)	109
		2.602(4)	3.519(4)			118.5(4)		
$Bn_2Yb(THP)_4$ (**129**)	κ¹-C	2.618(3)	3.495(3)	–	–	115.9(1)	93.0(3)	110
$Bn_2Yb(DME)_2$ (**131**)	η²-CC	2.572(4)	2.942(9)	–	–	90.8(4)	97.1(3)	110
		2.585(4)	3.172(2)			100.7(1)		
$Bn_2Ca(Me_4TACD)$ (**132**)	κ¹-C	2.639(3)	3.296(3)	–	–	104.2(3)10	83.3(3)	111
$Bn_2Ca(TMTA)_2$ (**142**)	κ¹-C	2.615(2)	3.380(2)	–	–	111.0(2)	98.1(2)	112
		2.631(2)	3.442(2)			113.0(2)		
$[Bn_4Sr_2(THF)_3]_n$ (**126**)	η³-CCC	2.691(2)	3.003(2)	3.135(2)	–	88.7(2)	–	113
	μ²- κ¹-C:η²-CC	2.817(2) ÷ 2.886(2)	2.954(2) ÷ 2.959(2)	–	–	–	–	
	μ²-κ¹-C:η⁶	2.806(2)	–	–	2.907(2) ÷ 3.305(2)	112.1(2)	–	
$[Bn_4Sm_2(THP)_2(THF)]_n$ (**135**)	η³-CCC	2.704(3)	3.032(3)	3.149(3)	–	90.6(3)	–	110
	μ²- κ¹-C:η²-CC	2.830(3) ÷ 2.903(3)	2.917(3) ÷ 2.920(3)	–	–	–	–	
	μ²-κ¹-C:η⁶	2.782(3)	–	–	2.877(3) ÷ 3.243(3)	109.7(3)	–	
$[Bn_8Eu_4(THF)_2]_n$ (**136**)	μ²- η³:η³-CCC	2.753(8) ÷ 2.888(7)	2.908(7) ÷ 3.251(8)	2.993(7) ÷ 3.380(7)	–	–	–	94
	μ²-κ¹-C:η⁶	2.837(7)	–	–	2.912(7) ÷ 3.183(7)	116.6(6)	–	
$[Bn_6Ba_3(THF)_4]_n$ (**127**)	μ²- κ¹-C:η²-CC	3.054(2) ÷ 3.090(2)	3.067(2) ÷ 3.104(2)	–	–	–	–	113
	μ²-κ¹-C:η⁶	2.963(2)	–	–	3.188(2) ÷ 3.249(2)	109.8(2)	–	

Scheme 38, Table 7). Schuhknecht *et al.*[111,116] demonstrated that THF molecules coordinated to metal ions in complexes $Bn_2M(THF)_n$ can be replaced with a tetradentate macrocyclic ligand Me_4TACD (1,3,5,7-tetramethyl-1,3,5,7-tetraazacyclododecane) to afford the corresponding adducts $Bn_2M(Me_4TACD)$ **132**, **133** (see Scheme 38, Table 7).

Scheme 38

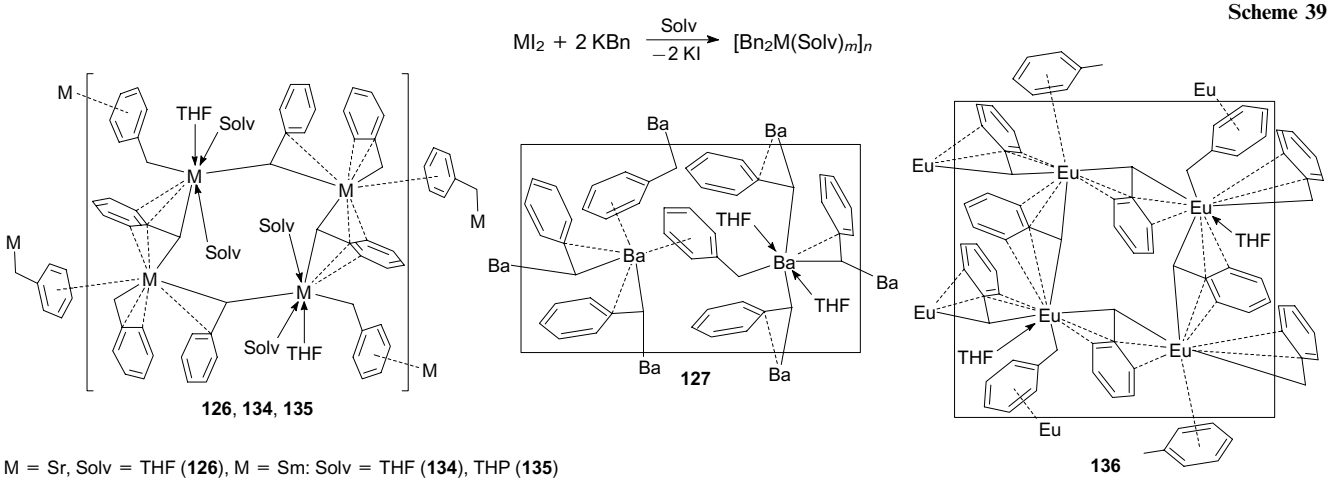


It should be noted that only in the case of Yb(II) complex **131**, which contains the least bulky bidentate molecules of 1,2-dimethoxyethane (DME) in the metal coordination sphere, short contacts between the Yb(II) ion and *ipso*-carbons of phenyl rings [2.942(9) – 3.172(2) Å] were found, indicating the presence of non-bonded interactions (see Table 7).

For metals with large ionic radii [Sr(II) 1.18 Å, Sm(II) 1.15 Å, Eu(II) 1.14 Å, Ba(II) 1.35 Å], the exchange reactions of MI_2 with KBn (1 : 2) in THF also proceed to give dibenzyl derivatives, which were isolated in the crystalline state as coordination polymers **126**, **127**,[113] **134**, **135**,[110] and **136**,[94] (Scheme 39). The authors note that despite the use of solvating solvents (THF or THP) in the exchange reactions, large ionic radii of Sr, Sm, Eu, and Ba, and also the oxophilicity of the ions of these elements, η^n-coordination of benzyl ligands in the resulting dibenzyl derivatives **126**, **127**, **134** – **136** is preferable as compared to the coordination of oxygen atoms of Lewis bases (see Table 7).

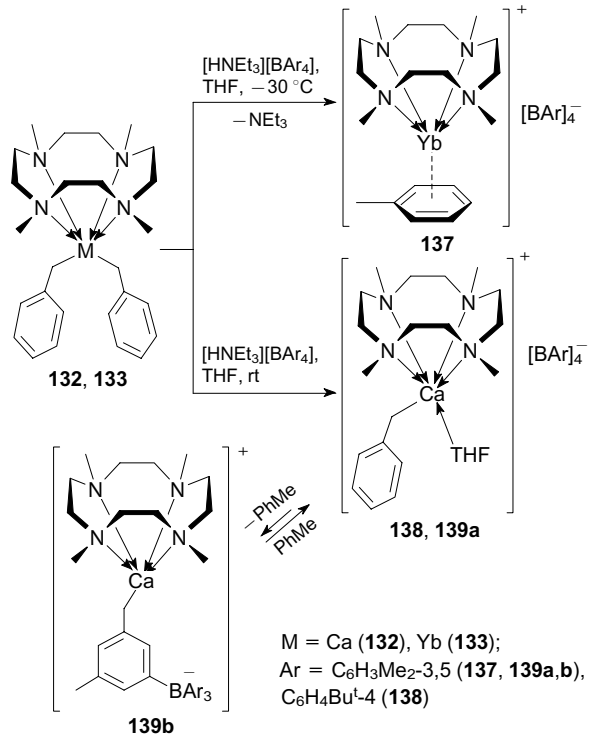
Schuhknecht *et al.*[111,116] employed dibenzyl derivatives of Ca **132** and Yb(II) **133** for the synthesis of cationic benzyl complexes. The reaction of **133** with $[HNEt_3][BAr_4]$ proceeds with the protonolysis of one of the M – C bonds, elimination of toluene, and affords the corresponding cationic benzyl complex **137** (Scheme 40).[116] X-ray diffraction data indicate η⁶-coordination of the phenyl ring of the benzyl ligand to the Yb(II) cations [Yb···C(Ar) 2.724(6) – 2.810(6) Å] in the resulting complex. The similar reactions of dibenzyl Ca complex **132** furnishes cationic benzyl complexes **138**, **139** (see Scheme 40).[111] The authors argue that Ca complex **138** is stable in the THF solution

Scheme 39



M = Sr, Solv = THF (**126**), M = Sm: Solv = THF (**134**), THP (**135**)

Scheme 40

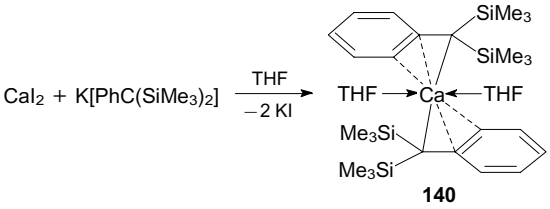


M = Ca (**132**), Yb (**133**);
Ar = $C_6H_3Me_2$-3,5 (**137**, **139a**,**b**), $C_6H_4Bu^t$-4 (**138**)

over several days, whereas for complex **139a**, elimination of toluene due to activation of the C−H bond of one of the methyl groups of the borate anion $[BAr_4]^-$ with benzyl anion was observed. The reaction gives a zwitterionic benzyl compound $[(Me_4TACD)Ca(CH_2C_6H_3Me\text{-}5\text{-}BAr_3)]$ (**139b**), isolated in 10% yield.

Feil and Harder[114] employed benzyl ligand $[PhC(SiMe_3)_2]^-$ bearing two $SiMe_3$ groups at the methanide carbon atom. It was found that an exchange reaction of CaI_2 with two equivalents of $K[PhC(SiMe_3)_2]$ gave dibenzyl complex $[(Me_3Si)_2CPh]_2Ca(THF)_2$ (**140**) (Scheme 41). X-ray diffraction analysis showed that the presence of two $SiMe_3$ groups at the α-carbon of the benzyl ligands changes its coordination mode from κ^1-CH_2, which is typical of the calcium benzyl complexes with unsubstituted benzyl carbanions, to the η^3-type due to the bonding of the metal centre to the α-CH_2 carbanionic atom, and also due to non-

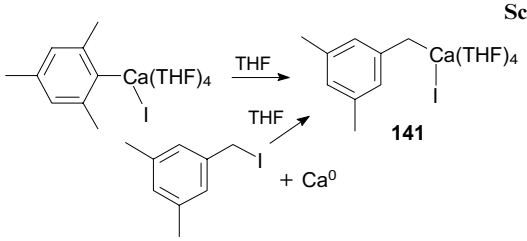
Scheme 41



bonded interactions with *ipso*- and *ortho*-carbons of the phenyl ring.

The formation of a benzyl derivative $(3,5\text{-}Me_2C_6H_3CH_2)CaI(THF)_4$ (**141**) was observed on a prolonged storage of aryl iodide complex $(2,4,6\text{-}Me_3C_6H_2)CaI(THF)_4$ (Scheme 42).[115] In this case, a straightforward reaction of the calcium metal with $3,5\text{-}Me_2C_6H_2CH_2I$ in THF affords complex **141** in the yield of as low as 15% since the Wurtz product dominates in this reaction.

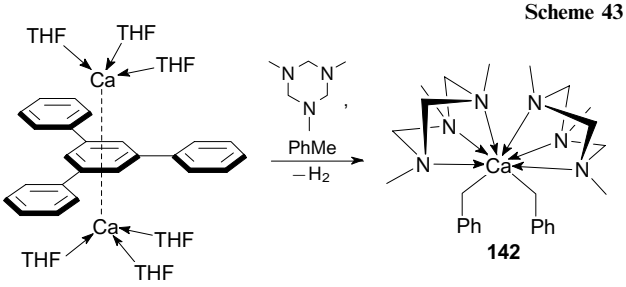
Scheme 42



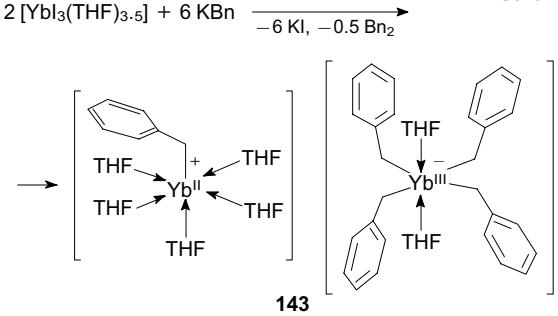
The formation of dibenzyl calcium complex $Bn_2Ca(TMTA)_2$ (**142**) was shown to occur due to metallation of toluene under the action of a superbasic bimetallic inverse sandwich Ca(I) complex $[(THF)_3Ca(\mu\text{-}C_6H_3\text{-}1,3,5\text{-}Ph_3)Ca(THF)_3]$ in the presence of 1,3,5-trimethyl-1,3,5-triazine (TMTA) (Scheme 43).[112]

In an attempted synthesis of tribenzyl Yb(III) complex *via* an exchange reaction of $YbI_3(THF)_{3.5}$ with 3 equivalents of KBn, a partial reduction of Yb(III) to Yb(II) occurred to give a mixed-valence complex $[Yb^{II}Bn(THF)_5]^+[Yb^{III}Bn_4(THF)_2]^-$ (**143**) (Scheme 44).[117] Complex **143** is a solvent-separated ion pair, the cationic part of which contains the Yb(II) ion covalently bonded to a

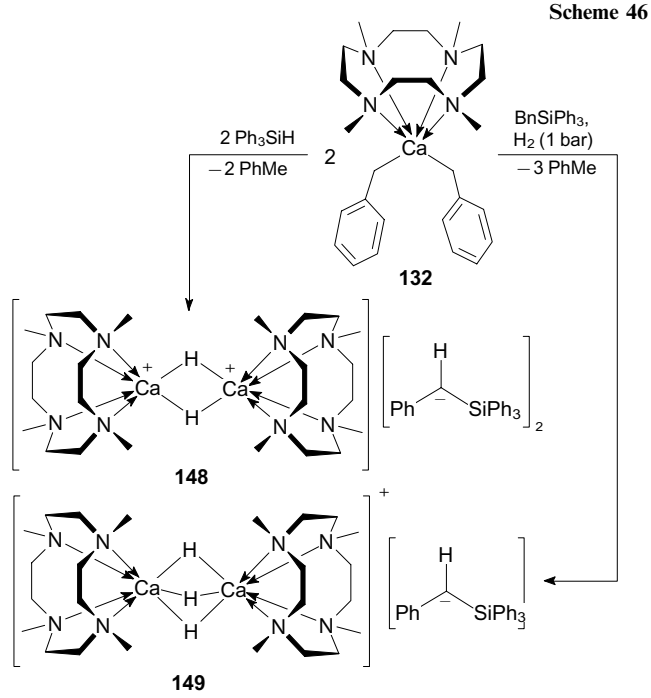
Scheme 43



Scheme 44



Scheme 46



benzyl ligand in the κ^1-CH_2 mode [Yb–CH_2: 2.566(14) Å] and five coordinated THF molecules. The anionic part is represented by a Yb(III) cation covalently bonded to four benzyl groups and two coordinated THF molecules.

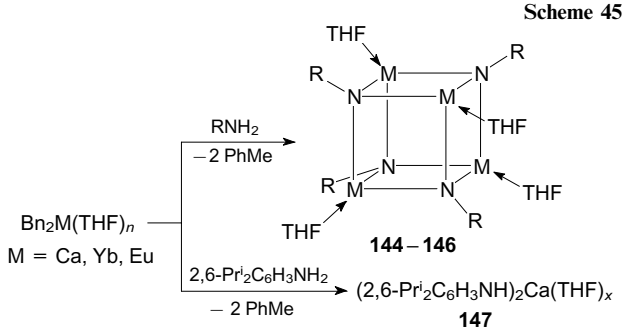
Benzyl derivatives of Ca, Yb, and Eu show high reactivity and can accomplish double deprotonation of the NH_2 groups in 2,6-$Pr^i_2C_6H_3NH_2$ and Ph_3SiNH_2 to provide the little-known imide complexes of Ln(II) and Ca. The reaction of $Bn_2M(THF)_n$ (M = Yb, Eu) with 2,6-diisopropylaniline (H_2NDipp) gives tetrameric imide complexes [(μ^3-NDipp)Ln(THF)]$_4$ **144**, **145** (Scheme 45).[110] The resulting complexes featured a cubane-like cage, in which four metal ions were linked by four μ^3-bridging imide $[RN]^{2-}$ ligands. Similar tetrameric imide calcium complex [(μ^3-NSiPh$_3$)Ca(THF)]$_4$ (**146**) was obtained *via* the reaction between Ph_3SiNH_2 and $Bn_2Ca(THF)_4$.[118] It is noteworthy that in the reaction of $Bn_2Ca(THF)_4$ with aniline 2,6-$Pr^i_2C_6H_3NH_2$, single deprotonation of the NH_2 moiety takes place to give bis(anilide) complex (2,6-$Pr^i_2C_6H_3NH)_2$Ca (**147**) (see Scheme 45).

When complex **132** was reacted with Ph_3SiH, dimeric dicationic hydride **148** was obtained, containing two silylated benzyl anions $[PhCHSiPh_3]^-$ as counterions (Scheme 46).[111,116] Hydrogenolysis of complex **132** under the action of H_2 in the presence of $PhCH_2SiPh_3$ is accompanied by the formation of monocationic hydride complex **149**.

Hydrogenolysis of cationic benzyl complexes **137**–**139** with molecular hydrogen also provides dimeric dicationic hydrides [(Me$_4$TACD)Yb(μ-H)$_2$Yb(THF)(Me$_4$TACD)]$^{2+}$[BAr$_4$]$_2^-$ **150**–**152** (Scheme 47).[111,116] In this case, tetraarylborate anions $[BAr_4]^-$ act as counterions.

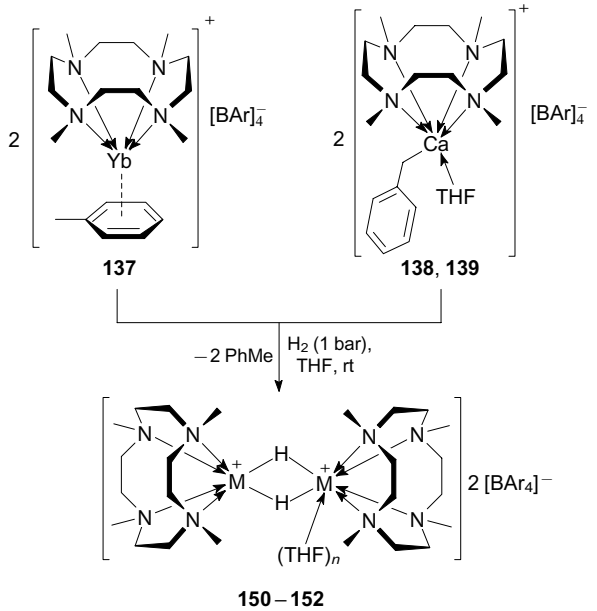
A series of heteroleptic benzyl complexes is known. The treatment of $Bn_2Ca(THF)_n$ with 1,4,7-trimethyl-

Scheme 45



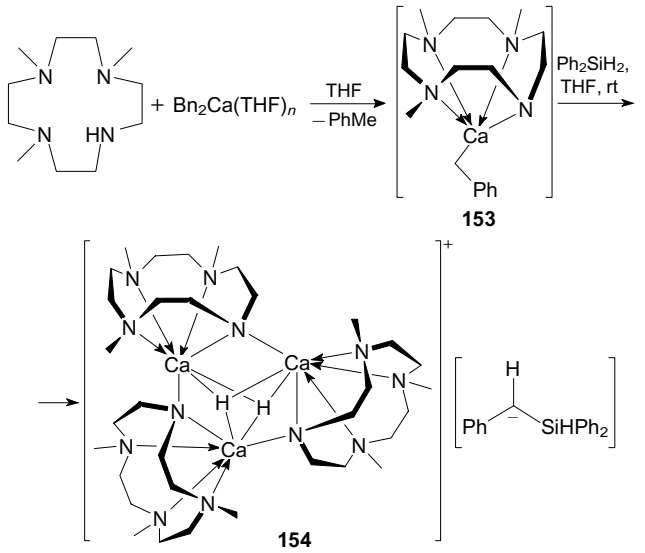
R = $C_6H_3Pr^i_2$-2,6: M = Yb (**144**), Eu (**145**);
R = $SiPh_3$, M = Ca (**146**)

Scheme 47



Ar = $C_6H_3Me_2$-3,5 (**137**, **139**, **150**, **151**), $C_6H_4Bu^t$-4 (**138**, **152**);
M = Yb (n = 1, **150**), Ca (n = 0, **151**, **152**)

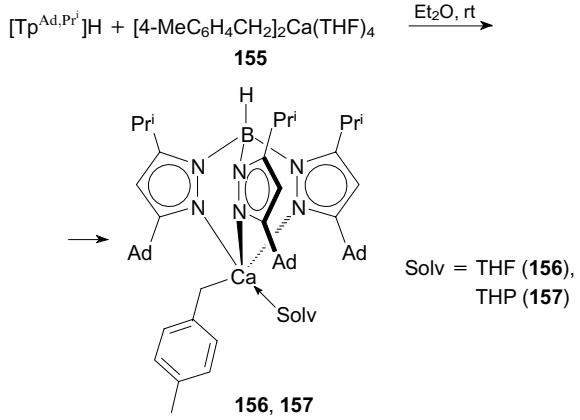
Scheme 48



1,4,7,10-tetraazacyclododecane [(Me_3TACD)H] afforded the corresponding monobenzyl complex [(Me_3TACD)CaBn]$_n$ (**153**) (Scheme 48).[119] The reaction of intermediate species **153** with Ph_2SiH_2 proceeds with activation of the CH bond of the newly formed Ph_2SiHBn and affords cationic hydride complex [{(Me_3TACD)Ca}$_3$(μ-H)$_2$][$Ph_2SiHCHPh$] (**154**), bearing silyl-substituted benzyl anion [$Ph_2SiHCHPh$]$^-$.

Through the action of [Tp^{Ad,Pr^i}]H on [4-$MeC_6H_4CH_2$]$_2$Ca(THF)$_4$ (**155**), stable benzyl calcium complexes in the form of adducts with THF or THP [Tp^{Ad,Pr^i}]Ca($CH_2C_6H_4$Me-4)(Solv) **156**, **157** were obtained (Scheme 49).[66]

Scheme 49



The reaction of (4-$Bu^tC_6H_4CH_2$)$_2$Ca(THF)$_4$ (**130**) with 2,3,4,5-pentakis(4-*tert*-butylphenyl)-1,3-cyclopentadiene ([Cp^{BIG}]H) did not result in isolation of a half-sandwich complex [Cp^{BIG}]CaBn (Scheme 50).[120] The authors note that despite the large bunk of cyclopentadienyl ligand [Cp^{BIG}], the Schlenk equilibrium is shifted towards the symmetrical products, namely, calcium bis(cyclopentadienide) [Cp^{BIG}]$_2$Ca (**158**) and the starting complex **130**. Orzechowski *et al.*[121] used the reaction between two equivalents of [Cp^{BIG}]H and $Bn_2Ba(THF)_n$ as a convenient approach to obtain the corresponding sandwich barium derivative [Cp^{BIG}]$_2$Ba (**159**).

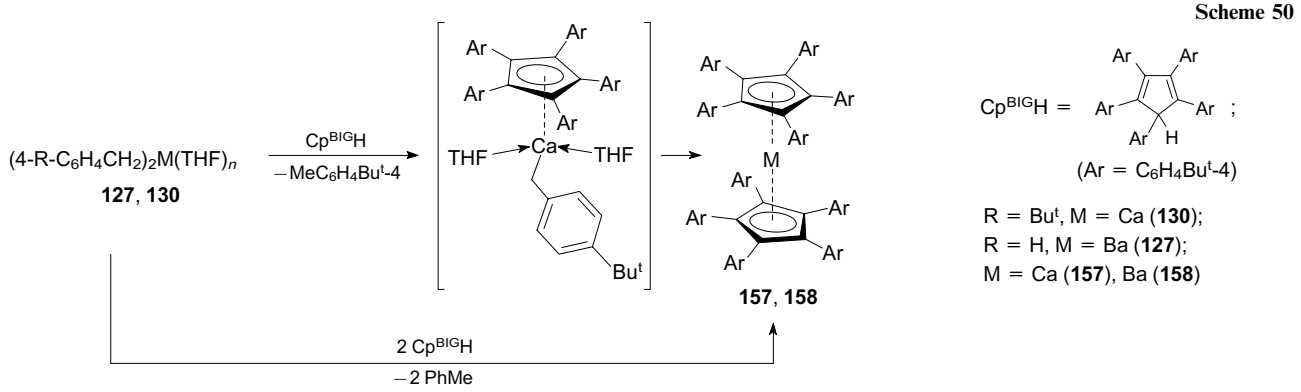
The reaction of *trans*-stilbene with hydride {[BDI]Ca(μ-H)}$_2$ gave a binuclear benzyl-hydride complex {[BDI]Ca(μ-H)(μ-$PhCHCH_2$Ph)Ca[BDI]} (**160**) (Scheme 51).[64] In complex **160**, the dimeric structure is formed by one bridging hydride ligand and bridging benzyl carbanion, which is bonded to one the calcium atom through the benzyl carbon atom and coordinated to the other calcium atom *via* the phenyl ring in the η^6-mode. The monomeric hydride calcium complex [Tp^{Ad,Pr^i}]CaH(THP) also adds across the C=C bond of *trans*-stilbene to afford complex [Tp^{Ad,Pr^i}]Ca[CH(Ph)Bn] (**161**) (see Scheme 51), in which the calcium atom is coordinated to the substituted benzyl ligand [BnCHPh]$^-$ in the η^3-mode.[66]

The addition of {[BDI]Ca(μ-H)}$_2$ to diphenylacetylene gives a tetranuclear complex {[BDI]Ca}$_4$(μ-H)$_2$[PhCHCHPh] (**162**), which is formed *via* double addition of the Ca – H bonds across the C≡C triple bond (Scheme 52).[64] Complex **162** contains a dianionic dibenzyl ligand [PhCH – CHPh]$^{2-}$, which is coordinated to four calcium ions. In this case, the interaction with two calcium ions occurs through the coordination of two carbanionic benzyl carbon atoms and one *ipso*-carbon of the phenyl ring of the ligand. Two remaining calcium ions are linked to the carbon atoms of the phenyl ring in the η^6-coordination mode.

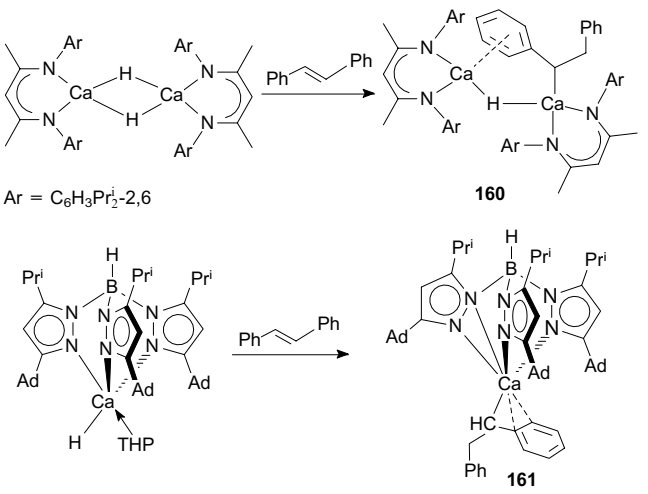
The formation of dianionic dibenzyl ligand [PhCH – CHPh]$^{2-}$ was observed in the reaction of diphenylacetylene with Ca and Yb(II) dimeric hydride complexes of {[Amd]M(μ-H)}$_2$, bearing amidinate ligands $Bu^tC(NC_6H_3Pr^i_2$-2,6)$_2$ (Amd). However, in this case, the resulting complexes {[Amd]M}$_2$[μ-PhCHCHPh] **163**[122] and **164**[123] are dimers in which two metal centres are bridged by dianion [PhCH – CHPh]$^{2-}$ in the η^4-mode (see Scheme 52).

The chemistry of benzyl derivatives gained a new impetus due to the employment of *o*-dimethylaminobenzyl

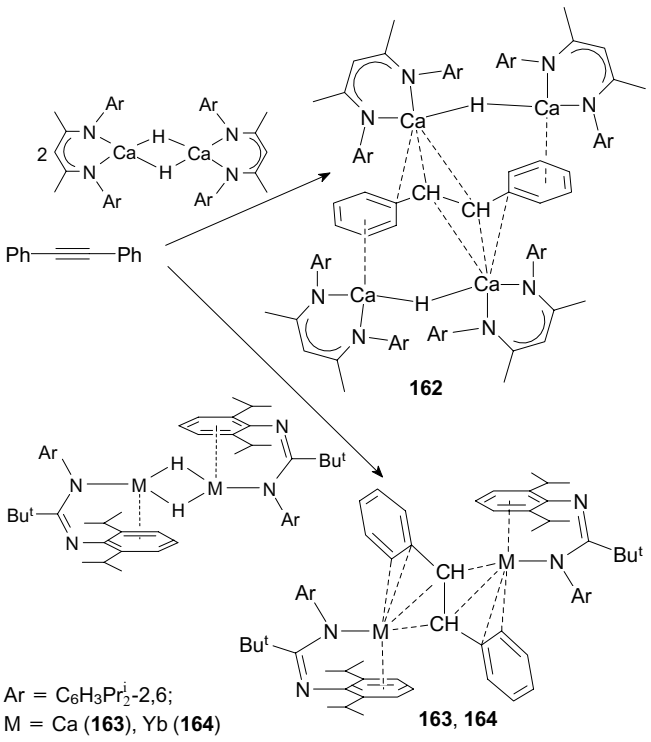
Scheme 50



Scheme 51



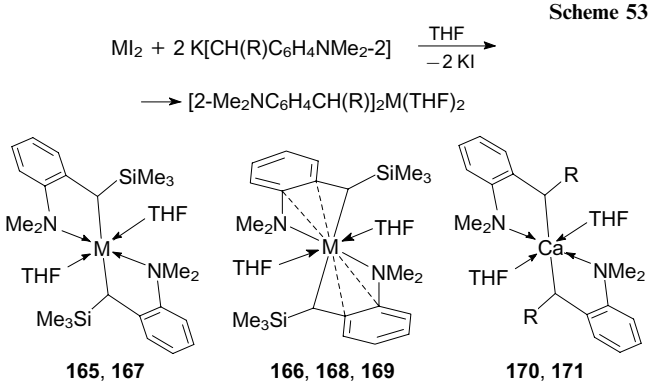
Scheme 52



ligands $[CH(R)C_6H_4NMe_2\text{-}2]$, bearing a donor NMe_2 group in the *ortho*-position of the phenyl ring. A series of complexes $[2\text{-}Me_2NC_6H_4CH(SiMe_3)]_2M(THF)_2$ **165**,[124] **166**,[125] **167**,[48] **168**,[48] **169**,[126] and $[o\text{-}Me_2NC_6H_4CH(R)]_2Ca(THF)_2$ **170**,[127] **171**[128] was obtained *via* the exchange reactions of MI_2 with two equivalents of $K[CH(R)C_6H_4NMe_2\text{-}2]$ (Scheme 53).

The coordination mode of the benzyl ligand was shown to depend on the ionic radius of the central metal ion. For metals with small radii [Ca, Yb(II)], *o*-dimethylaminobenzyl ligands attach to the metal centres in the κ^2-C,N mode by a covalent bond to the benzyl carbon atom and coordinate bond to the nitrogen atom of the NMe_2 moiety. In the complexes of metals with large ionic radii (compounds **166**, **168**, and **169**), η^4-coordination mode of the $[2\text{-}Me_2NC_6H_4CH(SiMe_3)]$ ligand is realized since *ipso*- and *ortho*-carbons of the phenyl rings are involved in the interaction (Table 8).

Scheme 53



Bulky fluorenes react with *o*-dimethylaminobenzyl complexes of Ca and Yb(II), bearing Me_3Si or Me substituents at the benzyl α-carbon atom, to furnish heteroleptic complexes **172**,[129] **173**,[48] **174** – **176**,[130] **177**,[127] **178**,[130] and **179**[127] (Scheme 54, Table 9). Using calcium complexes containing unsubstituted *o*-dimethylaminobenzyl ligands, dimeric derivatives **180**,[128] **181**[130] were obtained. The use of fluorene substituted in the 9-position with $(CH_2)_2NMe_2$ moiety also affords a half-sandwich calcium complex **182** (see Scheme 54, Table 9).[130]

Table 8. Selected interatomic distances (Å) and bond angles (deg.) in bis(*o*-dimethylaminobenzyl) complexes $[2\text{-}Me_2NC_6H_4CH(SiMe_3)]_2M(THF)_2$.

Complex	Coordination mode	M – C(α)	M···C(*ipso*)	M···C(*ortho*)	M – N	∠C – M – C	Dihedral angle MCN and CCCN	Ref.
$[2\text{-}Me_2NC_6H_4CH(SiMe_3)]_2Ca(THF)_2$ (**165**)	κ^2-C,N	2.618(3)	3.078(3)	3.080(3)	2.567(2)	157.5(3)	120.8(3)	124
		2.638(3)	3.080(3)	3.140(3)	2.632(2)		120.9(3)	
$[2\text{-}Me_2NC_6H_4CH(SiMe_3)]_2Yb(THF)_2$ (**167**)	κ^2-C,N	2.640(3)	3.069(3)	3.073(3)	2.577(2)	157.3(3)	119.1(3)	48
		2.661(3)	3.080(3)	3.133(3)	2.652(2)		119.5(3)	
$[2\text{-}Me_2NC_6H_4CH(SiMe_3)]_2Eu(THF)_2$ (**169**)	η^4-CCCN	2.763(3)	2.833(3)	2.842(3)	2.750(2)	142.7(3)	93.6(3)	126
		2.780(3)	2.939(3)	2.993(3)	2.764(2)		102.1(3)	
$[2\text{-}Me_2NC_6H_4CH(SiMe_3)]_2Sr(THF)_2$ (**166**)	η^4-CCCN	2.770(2)	2.862(2)	2.868(2)	2.759(2)	143.5(2)	94.1(2)	125
		2.798(2)	2.960(2)	3.019(2)	2.783(2)		103.2(2)	
$[2\text{-}Me_2NC_6H_4CH(SiMe_3)]_2Sm(THF)_2$ (**168**)	η^4-CCCN	2.768(3)	2.845(3)	2.845(3)	2.756(2)	142.5(3)	93.6(3)	48
		2.789(3)	2.938(3)	2.988(3)	2.771(2)		101.6(3)	

It was found that the reaction of complex **170** with fluorenyl ligand containing a sterically demanding $Si(SiMe_3)_3$ substituent in the 9-position is accompanied by activation of the methyl group at the silicon atom.[127] The reaction yields a binuclear derivative **183**, bearing a novel dianionic alkyl-fluorenyl ligand (Scheme 55).

In contrast to homoleptic dibenzyl Ca and Yb(II) derivatives characterized by the κ^2-C,N coordination of the *o*-dimethylaminobenzyl moieties, benzyl ligands in half-sandwich calcium complexes **172**, **174**, **177**, and **182** are attached to the metal centres in the η^4-CCCN mode.

Heteroleptic derivatives of Ca **172** and Yb(II) **173**, containing bulky fluorenyl ligands, proved to be stable in aromatic solvents; however, they undergo symmetrization in THF to give homoleptic bis(*o*-dimethylaminobenzyl) complexes **165**, **167**, and bis(fluorenyl) derivatives **185**, **186** (Scheme 56).[128]

To obtain a half-sandwich hydride derivative, Harder and Brettar[133] carried out the reaction of calcium complex **172** with phenylsilane. NMR monitoring data suggested the occurrence of the Ca – benzyl ligand σ-bond metathesis to afford $PhSiH_2CH(SiMe_3)C_6H_4NMe_2$-*o*. However, the generated hydride complex was unstable and decomposed to give bis(fluorenyl) derivative **185** and insoluble CaH_2 (Scheme 57).

Scheme 54

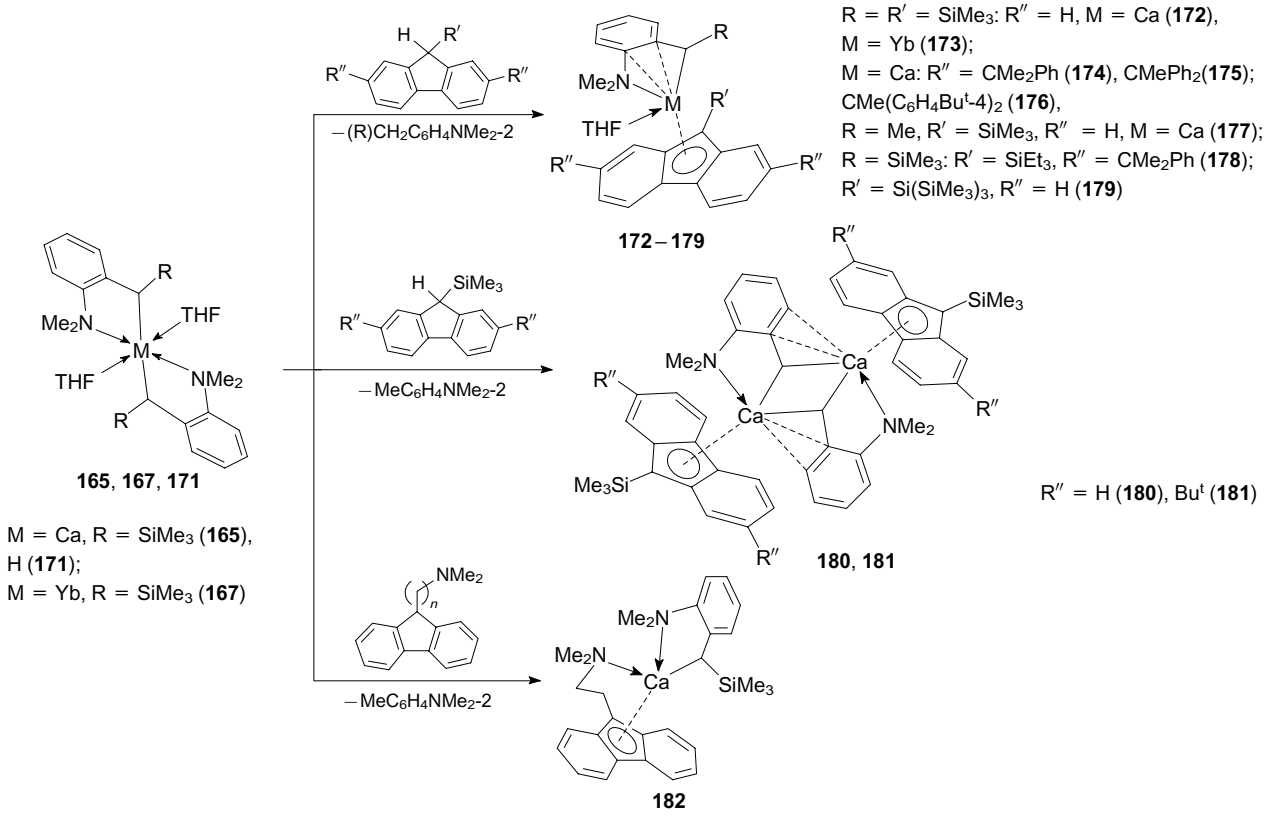
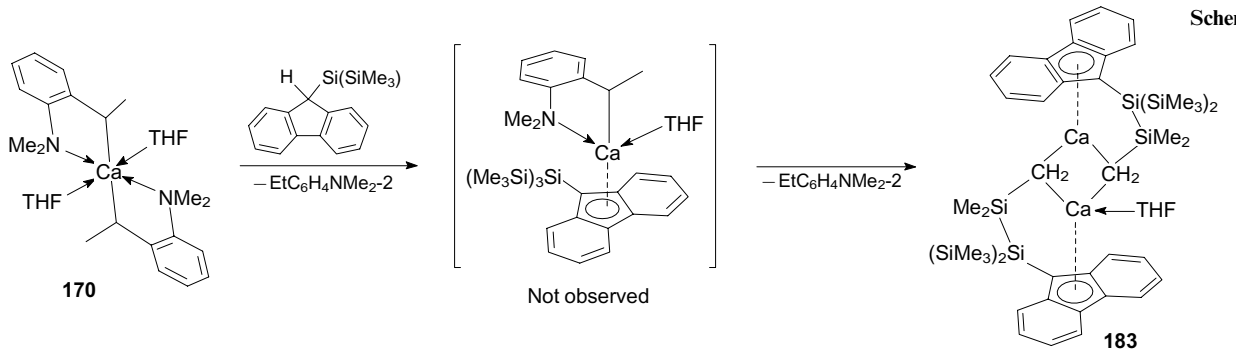


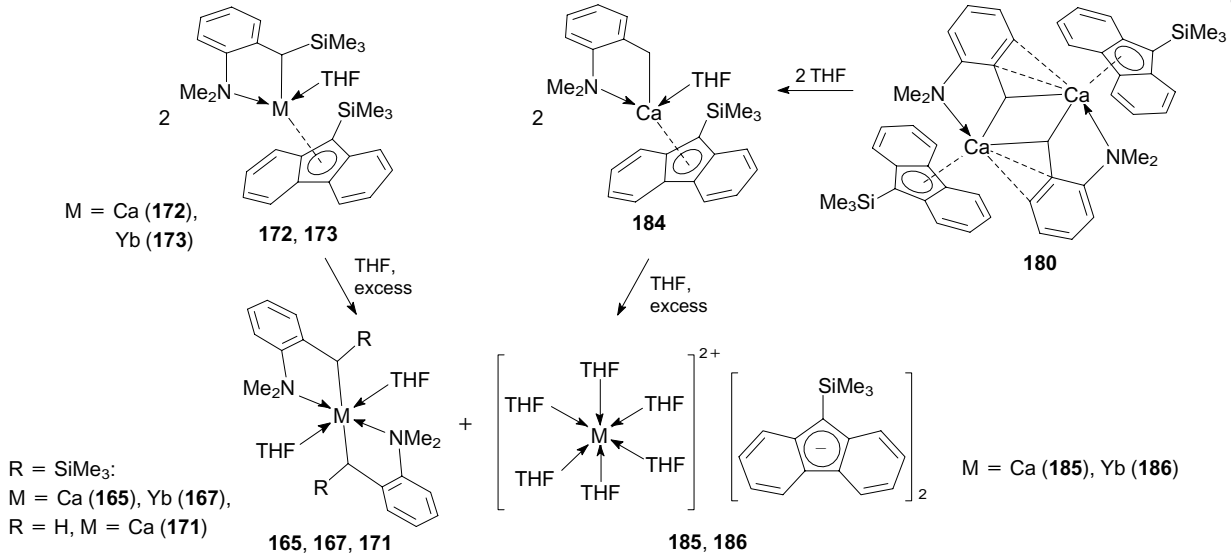
Table 9. Selected interatomic distances (Å) and bond angles (deg.) in heteroleptic *o*-dimethylaminobenzyl complexes $[L]M[CH(R)C_6H_4NMe_2\text{-}2](THF)_n$.

Complex	Coordination mode	M – C(α)	M···C (*ipso*)	M···C (*ortho*)	M – N	Dihedral angle MCN and CCCN	Ref.
$[9\text{-}Me_3Si\text{-}C_{13}H_8]Ca[CH(SiMe_3)C_6H_4NMe_2\text{-}2](THF)$ (**172**)	η^4-CCCN	2.510(3)	2.853(3)	2.897(3)	2.470(3)	114.3(3)	129
$[9\text{-}Me_3Si\text{-}C_{13}H_8]Ca[CH(Me)C_6H_4NMe_2\text{-}2](THF)$ (**177**)	η^4-CCCN	2.502(3)	2.789(3)	2.773(3)	2.451(3)	109.0(3)	127
$[2,7\text{-}PhMe_2C\text{-}9\text{-}Me_3Si\text{-}C_{13}H_6]Ca[CH_2C_6H_4NMe_2\text{-}2]$ (**174**)	η^4-CCCN	2.517(3)	2.776(3)	2.818(3)	2.496(3)	108.1(3)	130
$[9\text{-}Me_2N(CH_2)_2\text{-}C_{13}H_8]Ca[CH(SiMe_3)C_6H_4NMe_2\text{-}2](THF)$ (**182**)	η^4-CCCN	2.499(3)	2.790(3)	2.851(3)	2.465(3)	111.3(3)	128
$\{[9\text{-}Me_3Si\text{-}C_{13}H_8]Ca[CH_2C_6H_4NMe_2\text{-}2]\}_2$ (**180**)	κ^2-CN	M(1)2.571(4)	3.275(4)	3.286(4)	2.558(4)	138.8(4)	128
	η^3-CCC	M(2) 2.537(4)	2.806(4)	2.920(4)	–	–	
$\{[2,7\text{-}Bu^t\text{-}9\text{-}Me_3Si\text{-}C_{13}H_6]Ca[CH_2C_6H_4NMe_2\text{-}2]\}$ (**181**)	κ^2-CN	M(1) 2.572(4)	3.289(4)	3.311(4)	2.568(4)	141.6(4)	130
	η^3-CCC	M(2) 2.572(4)	2.888(4)	3.040(4)	–	–	
$[Me_4EtCp]Ca[\mu\text{-}CH_2C_6H_4NMe_2\text{-}2]$ (**187**)	κ^2-CN	M(1) 2.607(4)	3.229(4)	3.239(4)	2.600(4)	132.3(4)	128
	η^3-CCC	M(2) 2.621(4)	2.858(4)	2.863(4)	–	–	
$[Bu^t_4Carb]Sm[CH_2C_6H_4NMe_2\text{-}2](THF)_2$ (**188**)	η^4-CCCN	2.667(2)	2.949(2)	2.983(2)	2.713(2)	106.0(3)	131
$[BDI]Ca[CH_2C_6H_4NMe_2\text{-}2](THF)$ (**190**)	η^4-CCCN	2.650(3)	2.807(3)	2.877(3)	2.650(3)	104.7(3)	132
$[Tp^{Ad,Pr^i}]Ba[CH_2C_6H_4NMe_2\text{-}2]$ (**192**)	η^4-CCCN	2.877(4)	3.032(4)	3.089(4)	2.938(4)	98.6(4)	95

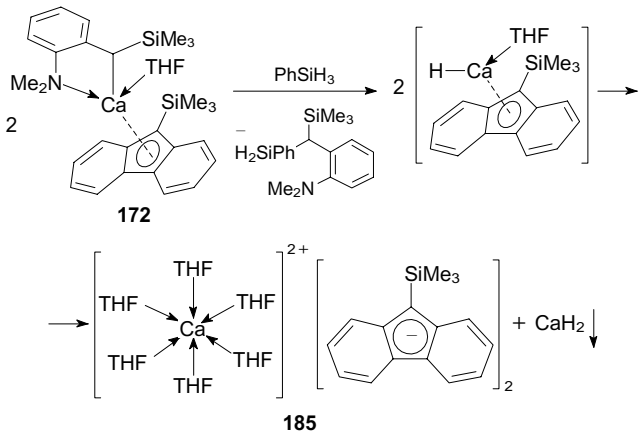
Scheme 55



Scheme 56



Scheme 57



The possibility to synthesize half-sandwich *o*-dimethylaminobenzyl complexes not only *via* protonolysis of the M–C bonds but also by desymmetrization reactions of homoleptic complexes $[L]_2M$ and $[2\text{-}Me_2NC_6H_4CH_2]_2Ca(THF)_2$, and the exchange reactions of heteroleptic halide complexes [L]MI with $K[CH_2C_6H_4NMe_2\text{-}2]$ has been demonstrated.[120, 128, 131, 134]

The reaction between $[Me_4EtCp]_2Ca$ and $[4\text{-}Me_2N\text{-}C_6H_4CH_2]_2Ca(THF)_2$ in benzene affords dimeric half-sandwich complex **187** (Scheme 58).[128] It is noteworthy that bis(cyclopentadienyl) calcium complex $[Cp^{BIG}]_2Ca$ does not exchange ligands with $[2\text{-}Me_2NC_6H_4CH(SiMe_3)]_2Ca(THF)_2$, which the authors attributed to the high stability of calcocene.[120]

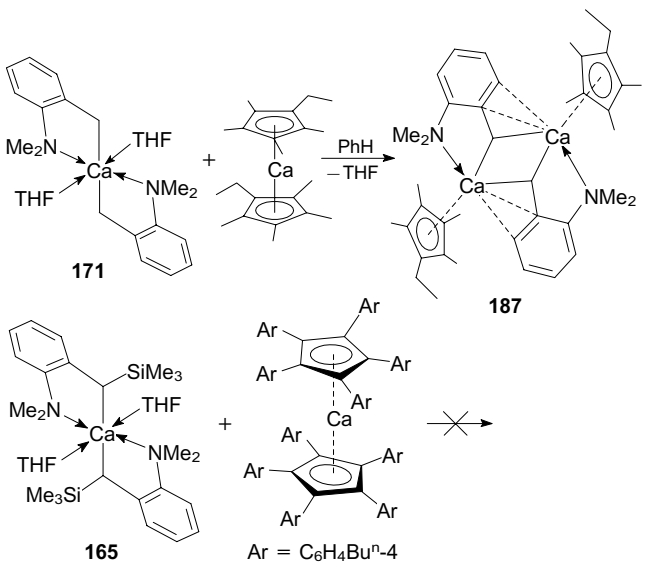
Selikhov *et al.*[131] have obtained complex $\{[Bu^t_4Carb]Sm[CH_2C_6H_4NMe_2\text{-}2](THF)_2$ (**188**), bearing 1,3,6,8-tetra(*tert*-butyl)-substituted carbazolyl ligand $[Bu^t_4Carb]$, by an exchange reaction of $\{[Bu^t_4Carb]Sm(\mu\text{-}I)(THF)_2\}_2$ with two equivalents of $K[CH_2C_6H_4NMe_2\text{-}2]$ (Scheme 59, see Table 9). The authors note that heteroleptic complex **188** is unstable and undergoes a total symmetrization in solution to afford a homoleptic derivative $[Bu^t_4Carb]_2Sm$ (**189**) (see Scheme 59, conditions *a*). The same compound was detected when attempting to synthesize the corresponding hydride complex on treating compound **188** with molecular hydrogen or $PhSiH_3$ (see Scheme 59, conditions *b*, *c*).

In contrast to carbazolyl iodide complex, the reaction of $\{[C_5Bn_5]Sm(\mu\text{-}I)(DME)\}_2$ with $K[CH_2C_6H_4NMe_2\text{-}2]$ (1 : 2) failed to provide the corresponding half-sandwich complex.[134]

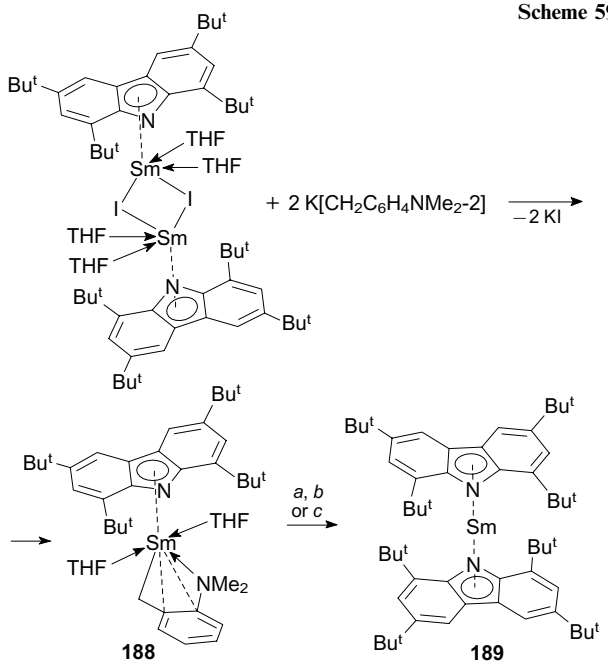
A series of works describe *o*-dimethylaminobenzyl derivatives containing polydentate β-diketoiminate and tris(pyrazolyl)borate ligands.[94, 101, 132, 135]

The reaction between equimolar amounts of $[2\text{-}Me_2NC_6H_4CH(SiMe_3)]_2Ca(THF)_2$ (**165**) and calcium bis(β-diketoiminate) $[BDI]_2Ca$ affords heteroleptic complex **190** (Scheme 60).[132] This complex is unstable in solution and at 50 °C undergoes an intermolecular activation of the CH bond of the methyl group of β-diketoiminate ligand to

Scheme 58



Scheme 59

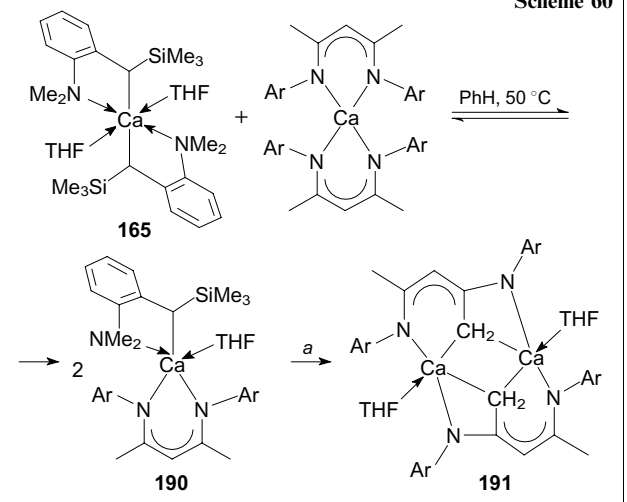


eliminate $(Me_3Si)CH_2C_6H_4NMe_2$-2 and to yield a dimeric aminomethylene Ca complex (**191**), bearing an azapentadienyl(azaallylic) dianion.

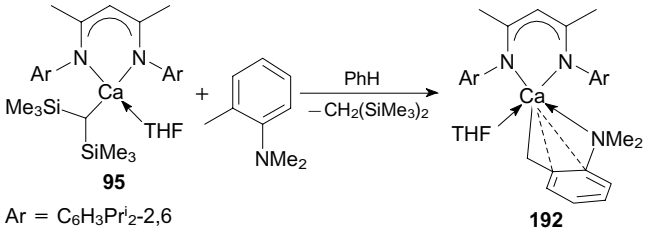
The transalkylation reaction of *ortho*-*N*,*N*-dimethyltoluidine with [BDI]Ca[$CH(SiMe_3)_2$](THF) furnished benzyl complex **192** (Scheme 61).[101] Unlike **190**, complex **192** is stable and does not decompose in solution at 60 °C.

An exchange reaction between complex $\{[BDI^{N,N}]Yb(\mu\text{-}I)\}_2$, containing a tetradentate β-diketoiminate ligand with one of the nitrogen atoms being substituted by a donor $(CH_2)_2N(Me)(CH_2)_2NMe_2$ group, with K[$CH_2C_6H_4NMe_2$-2] (1 : 2) opens access to *o*-dimethylaminobenzyl complex $[BDI^{N,N}]Yb[CH_2C_6H_4NMe_2\text{-}2]$ (**193**) (Scheme 62).[94]

Scheme 60

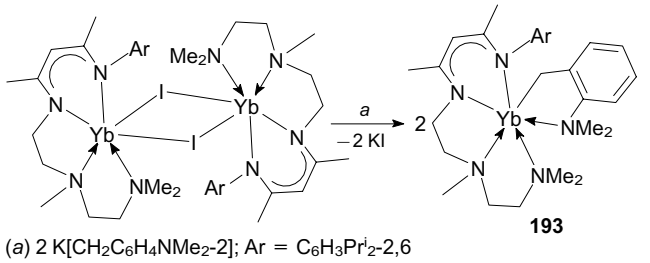


Scheme 61

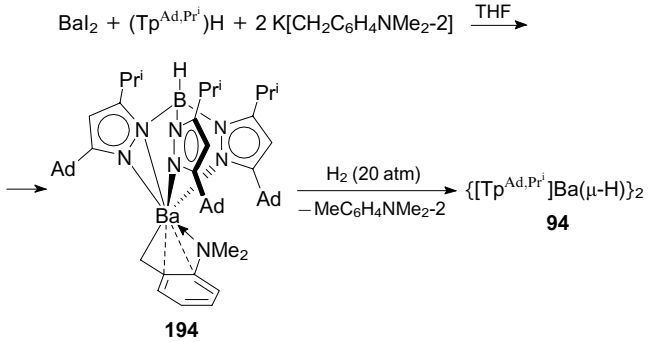


Barium complex $[Tp^{Ad,Pr^i}]Ba[CH_2C_6H_4NMe_2\text{-}2)]$ (**194**) was synthesized *via* the reaction of BaI_2, K[$CH_2C_6H_4NMe_2$-2], and $[Tp^{Ad,Pr^i}]H$ (1 : 2 : 1 molar ratio) in THF (Scheme 63).[135] As with *o*-dimethylaminobenzyl derivatives of Sr, Sm, and Eu, *o*-dimethylaminobenzyl ligand coordinates to the barium ion in the η^4-coordination mode. The authors have also mentioned that complex **194** is

Scheme 62



Scheme 63



stable in THF and aromatic solvents and can be employed in the synthesis of the corresponding hydride derivative $\{[Tp^{Ad,Pr^i}]Ba(\mu\text{-}H)\}_2$ through hydrogenolysis.

4.2. Diphenylmethyl complexes

The synthesis of diphenylmethyl barium complex $(Ph_2CH)_2Ba(THF)_n$ (**195**) was first reported in 2000.[108] As a result of higher acidity of the CH-bonds of the diphenylmethane methylene group (pK_a 32.3) compared to those of the toluene Me group (pK_a 43),[136] in the reaction of $Bn_2Ba(THF)_n$ (**127**) with Ph_2CH_2, toluene is eliminated to give bis(diphenylmethanide) **195** (Scheme 64). However, complex **195** was not obtained in an analytically pure form, but contained up to 12% of the starting dibenzyl complex **127**.

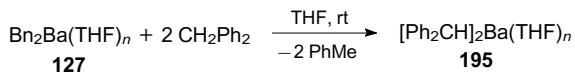
Later, it was shown that carrying out the transalkylation reaction of $Bn_2Ba(THF)_n$ with 2 equivalents of Ph_2CH_2 in the presence of $(Me_2N)_3P{=}O$ (HMPA), 18-crown-6 or in DME solution affords bis(diphenylmethyl)barium complexes $[Ba(HMPA)_6][CHPh_2]_2$ (**196**), $(Ph_2CH)_2Ba([18]$-crown-6) (**197**), and $(Ph_2CH)_2Ba(DME)_2$ (**198**) in 50 – 73% yields (Scheme 65).[137, 138] It was also established that complexes **196** – **198** can be synthesized by an exchange reaction between $[(Me_3Si)_2N]_2Ba(THF)_2$ and two equivalents of lithium diphenylmethanide $(Ph_2CH)Li(TMEDA)$.

Homoleptic bis(diphenylmethyl) derivatives of alkaline earth metals with smaller ionic radii (Ca, Sr) could not be obtained.[137, 138] The attempted synthesis of similar diphenylmethyl Sr complex *via* the reaction of $Bn_2Sr(THF)_n$ with Ph_2CH_2 in the presence of 18-crown-6 was accompanied by cleavage of the solvent (THF) and yielded dimeric heteroleptic enolate-diphenylmethyl derivative **199** (Scheme 66). The similar product **200** of the ethereal solvent cleavage is also formed upon storage of barium complex **197** in a concentrated solution of THF (see Scheme 66).

The outcome of the reaction between $[(Me_3Si)_2N]_2Ca(THF)_2$ and $(Ph_2CH)Li(TMEDA)$ was shown to be influenced by the solvent nature. In THF or DME, despite the use of two equivalents of lithium diphenylmethanide, only one amide group is substituted to give heteroleptic amido-diphenylmethyl complex **201** (Scheme 67).[138] In Et_2O, the reaction affords anionic tris(diphenylmethyl) derivative **202**.[139]

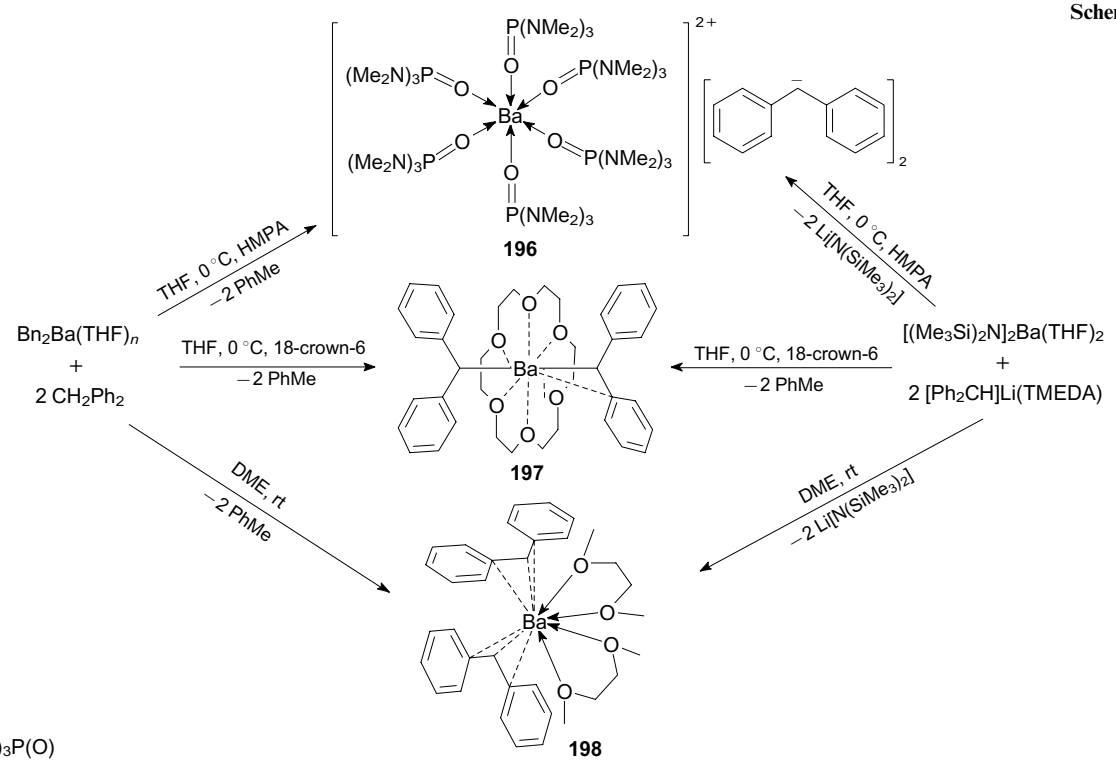
Enolate-diphenylmethyl derivatives **199**, **200**, and the amido-diphenylmethyl complex **201** are solvent-separated ion pairs. Conversely, in complex **202**, the calcium ion binds

Scheme 64



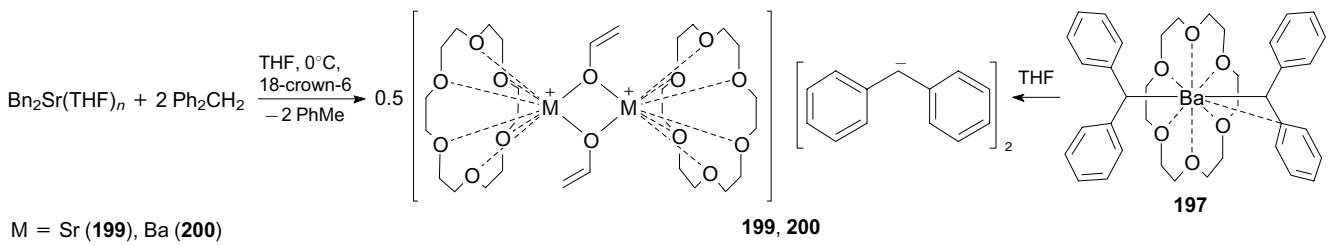
127 **195**

Scheme 65



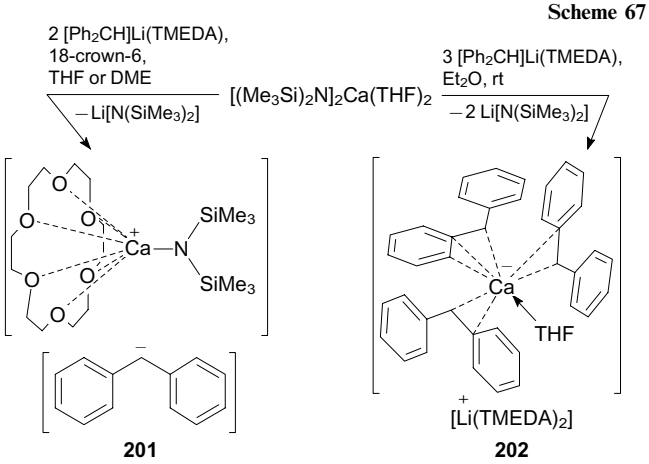
HMPA = $(Me_2N)_3P(O)$

Scheme 66



M = Sr (**199**), Ba (**200**)

Scheme 67



to three diphenylmethyl ligands, with their coordination mode being different (Table 10).

The first attempts to synthesize diphenylmethyl complexes based on an exchange reaction between YbI_2 and $KCHPh_2$ were performed by Schumann *et al.*[143] back in 2006. However, according to the authors, neither varying the reaction conditions nor the use of THF or DME as solvents gave the desired products.

Recently, the synthesis of diphenylmethyl complexes of Ca and Ln(II) (Ln = Yb, Sm) has been successfully carried out due to the use of bulky diphenylmethanide ligands $[(4\text{-}Bu^tC_6H_4)_2CH]^-$, substituted with *tert*-butyl groups in the *para*-positions of the phenyl rings of the diphenylmethane backbone.[140] The reaction of $MI_2(THF)_2$ [M = Ca, Yb(II), Sm(II)] with $Na[CH(C_6H_4Bu^t\text{-}4)_2]$ (1 : 2) opened access to the corresponding bis(diphenylmethyl) derivatives **203** – **207** in 55 – 80% yields (Scheme 68).

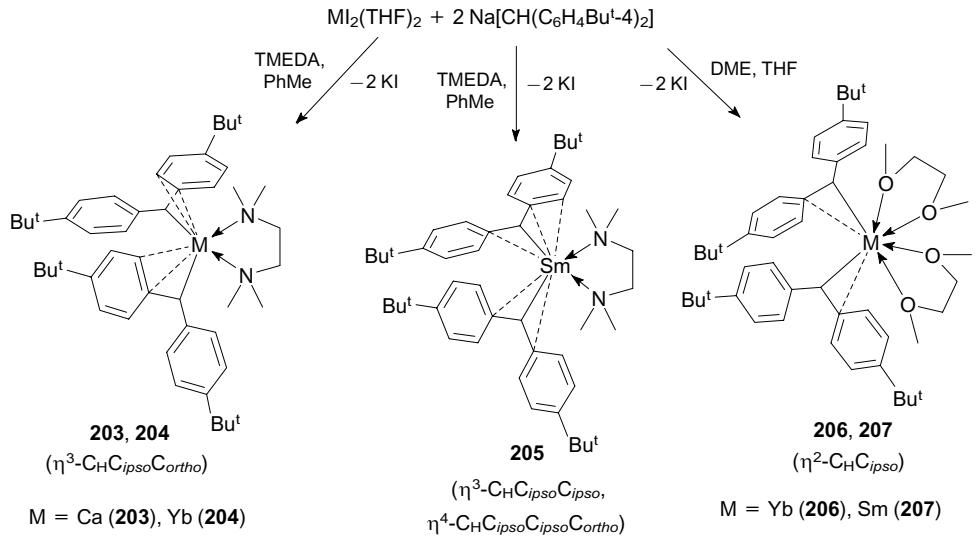
Complexes **203** – **205** and **207**, depending on the ionic radius of the metal centre and the number and nature of the coordinated Lewis bases, show various coordination patterns for diphenylmethyl ligands (see Table 10). In complexes of Ca **203** and Yb(II) **204**, the ligands are η^3-coordinated to the metal ions *via* the central methanide carbon and *ipso*- and *ortho*-carbons of one of the phenyl rings of each of diphenylmethyl carbanions. In Sm(II) complex **205** containing the metal ion with large ionic radius, the hapticity of bonding of one of diphenylmethyl ligands increases $\eta^3\text{-}C_HC_{ipso}C_{ortho}$ to $\eta^4\text{-}C_HC_{ipso}C_{ipso}C_{ortho}$ due to the interaction with *ipso*-carbon of the second phenyl ring.

Complexes **203** – **205** withstand heating in C_6D_6 to 100 °C for 72 h without any signs of decomposition. High thermal stability of complexes **203** – **207** stems from the absence of β-hydrogen atoms in diphenylmethyl ligands and inactivity of the coordinated Lewis base, TMEDA. In contrast, DME-adducts **206** and **207** are unstable and being heated in THF-d_8 solution at 75 °C for 8 h, decompose

Table 10. Selected interatomic distances (Å) and bond angles (deg.) in diphenylmethyl complexes.

Complex	Coordination mode	M – C(α)	M···C(*ipso*)	M···C(*ortho*)	∠C – M – C	Ref.
$(Ph_2CH)_2Ba$([18]crown-6) (**197**)	κ^1-C	3.096(3)	–	–	174.7(4)	137
	η^2-CC	3.065(3)	3.389(3)	–		
$(Ph_2CH)_2Ba(DME)_2$ (**198**)	$\eta^3\text{-}C_HC_{ipso}C_{ipso}$	2.902(4)	3.188(4) ÷ 3.302(4)	–	113.8(4)	138
	$\eta^3\text{-}C_HC_{ipso}C_{ortho}$	3.038(4)	3.028(4)	3.219(4)		
$[(Ph_2CH)_3Ca(THF)][Li(TMEDA)_2]$ (**202**)	$\eta^2\text{-}C_HC_{ipso}$	2.575(2) ÷ 2.587(2)	3.004(2) ÷ 3.100(2)	–	106.0(2) ÷ 116.4(2)	139
	$\eta^3\text{-}C_HC_{ipso}C_{ortho}$	2.612(2)	2.855(2)	2.935(2)		
$[(4\text{-}Bu^tC_6H_4)_2CH]_2Ca(TMEDA)$ (**203**)	$\eta^3\text{-}C_HC_{ipso}C_{ortho}$	2.545(2) ÷ 2.647(2)	2.622(2) ÷ 2.842(2)	2.871(2) ÷ 2.912(2)	118.7(2)	140
$[(4\text{-}Bu^tC_6H_4)_2CH]_2Yb(TMEDA)$ (**204**)	$\eta^3\text{-}C_HC_{ipso}C_{ortho}$	2.555(2) ÷ 2.668(2)	2.617(2) ÷ 2.853(2)	2.889(2) ÷ 2.896(2)	118.5(2)	140
$[(4\text{-}Bu^tC_6H_4)_2CH]_2Sm(TMEDA)$ (**205**)	$\eta^3\text{-}C_HC_{ipso}C_{ipso}$	2.863(2)	2.701(2)	2.962(2)	115.3(2)	140
	$\eta^4\text{-}C_HC_{ipso}C_{ipso}C_{ortho}$	2.662(2)	2.944(2) ÷ 2.999(2)	3.059(2)		
$[(4\text{-}Bu^tC_6H_4)_2CH]_2Sm(DME)_2$ (**207**)	$\eta^2\text{-}C_HC_{ipso}$	2.760(2)	3.065(2) ÷ 3.086(2)	–	103.3(2)	140
$[Bu^t_4Carb]Yb[CH(C_6H_4Bu^t\text{-}4)_2](TMEDA)$ (**208**)	κ^1-C	2.597(3)	–	–	–	141
$[Bu^t_4Carb]Yb[CH(C_6H_4Bu^t\text{-}4)_2](DME)$ (**209**)	$\eta^2\text{-}C_HC_{ipso}$	2.540(4)	2.806(4)	–	–	141
$[Bu^t_4Carb]Sm[CH(C_6H_4Bu^t\text{-}4)_2](DME)$ (**210**)	$\eta^3\text{-}C_HC_{ipso}C_{ipso}$	2.670(4)	2.904(3) ÷ 3.125(4)	–	–	141
[2,7-Bu^t-9-Me_3Si-$C_{13}H_6$]Yb[CH. .$(C_6H_4Bu^t\text{-}4)_2$](DME) (**211**)	$\eta^3\text{-}C_HC_{ipso}C_{ipso}$	2.589(2)	2.721(2)	2.737(2)	–	141
$[2,2'\text{-}(4\text{-}MeC_6H_3NMe_2)_2CH]_2Ca(THF)_2$ (**212**)	κ^2-CN	2.618(2) 2.637(2)	–	–	165.6(2)	142
$[2,2'\text{-}(4\text{-}MeC_6H_3NMe_2)_2CH]_2Ca$ (**213**)	$\kappa^1\text{-N-}\eta^4$-CCCN	2.546(3)	2.740(3)	2.862(3)	153.1(3)	142
		2.583(3)	2.719(3)	2.881(3)		
$[2,2'\text{-}(4\text{-}MeC_6H_3NMe_2)_2CH]_2Yb$ (**214**)	$\kappa^1\text{-N-}\eta^4$-CCCN	2.576(4)	2.730(4)	2.852(3)	152.1(4)	142
		2.585(4)	2.742(4)	2.864(4)		
$[2,2'\text{-}(4\text{-}MeC_6H_3NMe_2)_2CH]_2Sm$ (**215**)	$\kappa^1\text{-N-}\eta^4$-CCCN	2.710(2)	2.779(2)	2.854(2)	156.9(2)	142
		2.728(2)	2.804(2)	2.883(2)		

Scheme 68



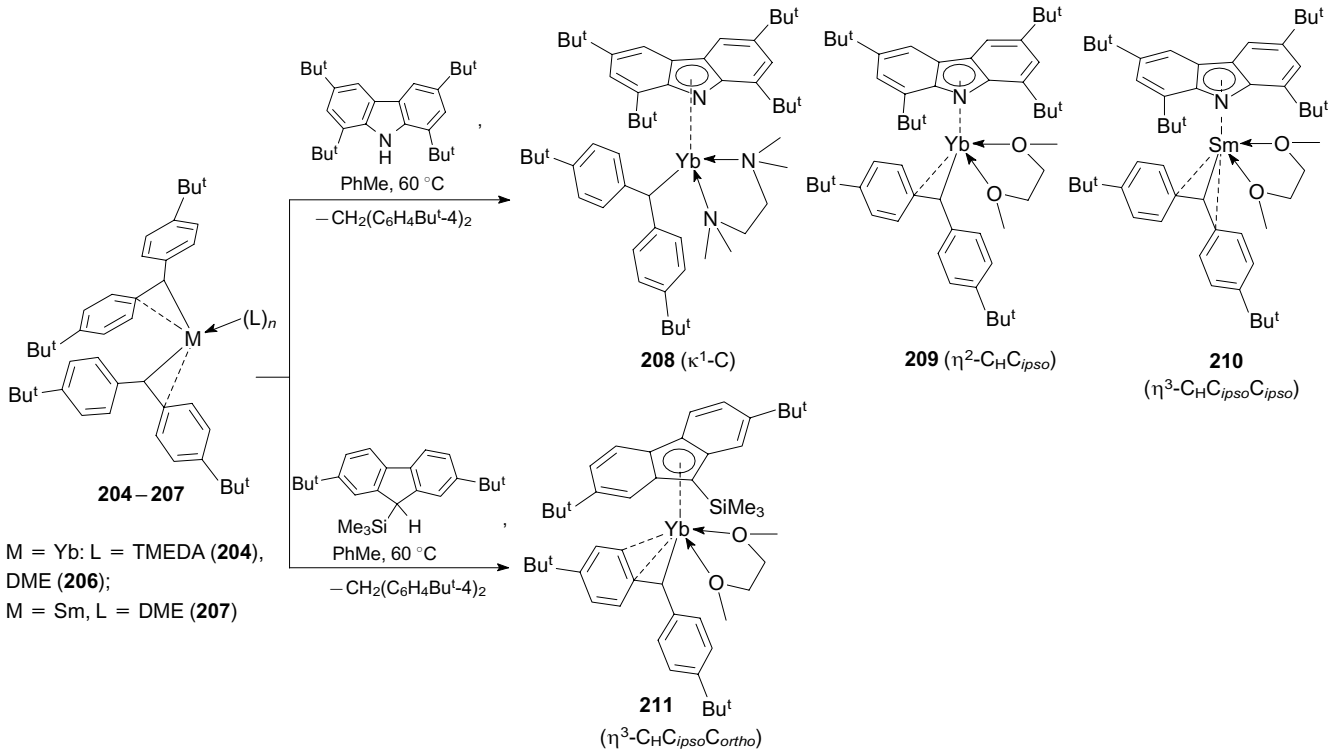
completely to give $CH_2(C_6H_4Bu^t\text{-}4)_2$ and $(4\text{-}Bu^tC_6H_4)_2CH(Me)$ (55 and 45%).

Complexes of Yb and Sm (**204**, **206**, and **207**) reacts with 1,3,6,8-tetra(*tert*-butyl)-9*H*-carbazole ($[Bu^t_4Carb]H$) to afford half-sandwich species **208**–**210** (Scheme 69).[141] The reaction between equimolar amounts of **204** and 2,7-di-*tert*-butyl-9-trimethylsilylfluorene proceeds similarly to give heteroligand complex **211**.

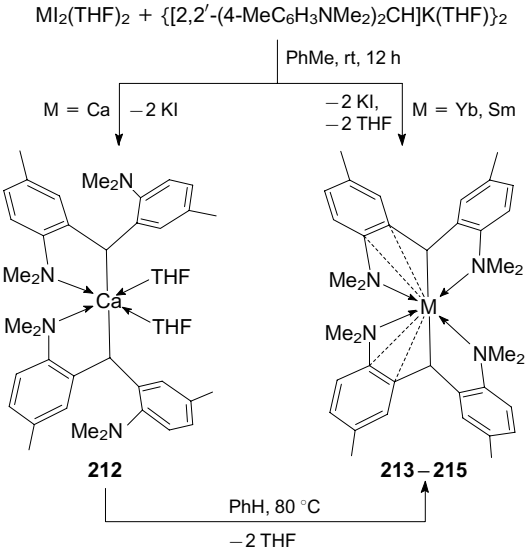
In constrast to the starting compound **204**, in complex **208**, diphenylmethyl ligand binds to the Yb(II) ion in the κ^1-C mode due to the covalent bond with the methanide carbon atom [Yb–C 2.597(3) Å]. Complexes **209** and **210**, containing less sterically demanding THF, demonstrate η^2- [for Yb(II) **209**] or η^3-coordination modes [for Sm(II) **210**]. In Yb(II) complex **211**, bearing a fluorene ligand, η^3-coordination of the diphenylmethyl moiety has also been observed.

Khristolyubov *et al.*[142] synthesized diphenylmethyl derivatives of Ca and Ln(II) (Yb, Sm) with the use of a tridentate diphenylmethyl ligand $[2,2'\text{-}(4\text{-}MeC_6H_3NMe_2)_2CH]^-$ (Ref. 144) substituted in *ortho*-positions of phenyl rings with NMe_2 donor groups, which can coordinate to a metal centre to form a pincer-type structure. For $CaI_2(THF)_2$, the reaction was shown to afford bis-(diphenylmethyl) complex $[2,2'\text{-}(4\text{-}MeC_6H_3NMe_2)_2CH]_2Ca(THF)_2$ (**212**) as an adduct with two THF molecules which can be converted into a non-solvated complex **213** on keeping **212** in benzene at 80 °C (Scheme 70). At the same time, the use of Yb(II) and Sm(II) diiodides makes it possible to obtain bis(diphenylmethyl)

Scheme 69



Scheme 70



M = Ca (**213**), Yb (**214**), Sm (**215**)

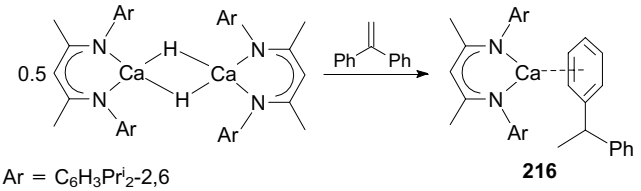
complexes **214**, **215**, free of coordinated THF. Mention has been made of the high thermal stability of diphenylmethyl complexes **212**, **215**: no evidence of decomposition was found even after heating their solutions in C_6D_6 at 80 °C for 5 days.

In complex **212**, both diphenylmethanide ligands are bidentate and coordinate to the metal atom *via* the covalent Ca – C and coordinate Ca – N bonds, whereas the second nitrogen atom of each of the ligands is rotated away from the metal centre and is not involved in complexation. In non-solvated complexes **213** – **215**, both diphenylmethanide ligands become tridentate and form [$NC_{sp^3}N$] pincer structure with two five-membered metallacycles MCCCN. Complexes **213** – **215** have tridentate [$NC_{sp^3}N$] pincer diphenylmethanide ligands coordinated to the metal centre in the κ^1-N-η^4-CCCN-mode.

The addition of hydride {[BDI]Ca(μ-H)}$_2$ to 1,1-diphenylethylene led to diphenylmethyl complex [BDI]Ca[C(Me)Ph$_2$] (**216**), in which the carbanion is bonded to the metal centre through η^6-coordination of carbon atoms of one of the phenyl rings (Scheme 71).[64] It has also been established that {[BDI]Ca(μ-H)(THF)}$_2$ reacts with diphenylethylene to afford the addition product as a THF adduct **217**.[146]

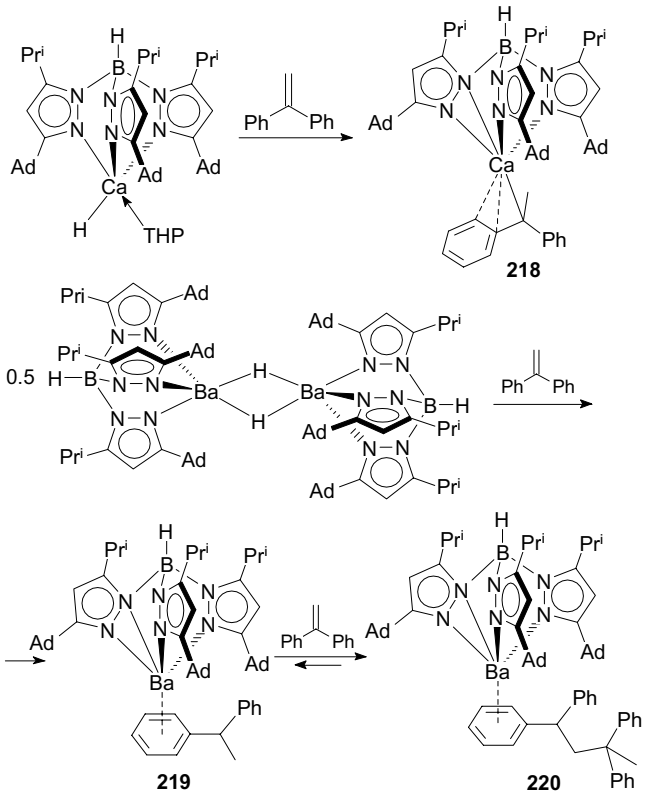
The addition of hydrides [Tp$^{Ad,Pr^i}$]CaH(THP) and {[Tp$^{Ad,Pr^i}$]Ba(μ-H)}$_2$ to 1,1-diphenylethylene proceeds in a similar way (Scheme 72). In this case, the structure of the newly formed diphenylmethyl complexes **218**,[66] **219**[146] depends on the ionic radius of the metal centre. For calcium, the addition product **218** shows η^3-coordination

Scheme 71



Ar = C$_6$H$_3$Pr$^i_2$-2,6

Scheme 72



mode of diphenylmethanide ligand. For barium complex **219**, having larger ionic radius of the metal centre, diphenylmethanide ligand coordinates to the metal centre in the η^6-mode. The second equivalent of 1,1-diphenylethylene, being added to complex **219**, led to insertion of alkene into the CH bond of the methyl group of the substituted diphenylmethyl ligand to furnish complex [Tp$^{Ad,Pr^i}$]Ba(η^6-Ph)C(Ph)-CH$_2$CMe(Ph)$_2$] (**220**), retaining η^6-coordination of the carbanion (see Scheme 72).[146] The authors note that the insertion of the second equivalent of 1,1-diphenylethylene is reversible and the addition of 40 equivalents of the alkene to {[Tp$^{Ad,Pr^i}$]Ba(μ-H)}$_2$ in C_6D_6 solution provides a mixture of complexes **219** and **220** in the ratio of 1 : 7 within 6 days.

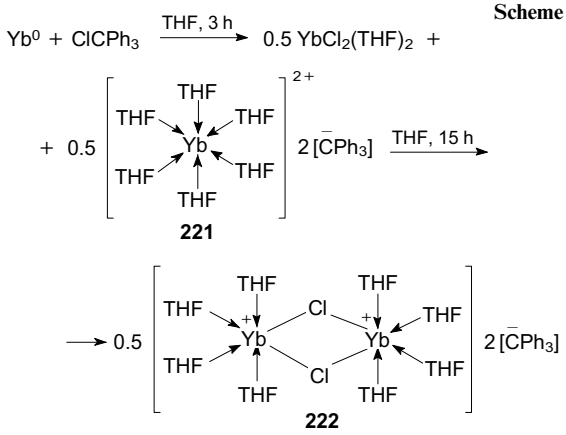
4.3. Triphenylmethanide complexes

In contrast to benzyl and diphenylmethanide deriatives, triphenylmethanide derivatives [Ph$_3$C]$^-$ are mostly ionic compounds.

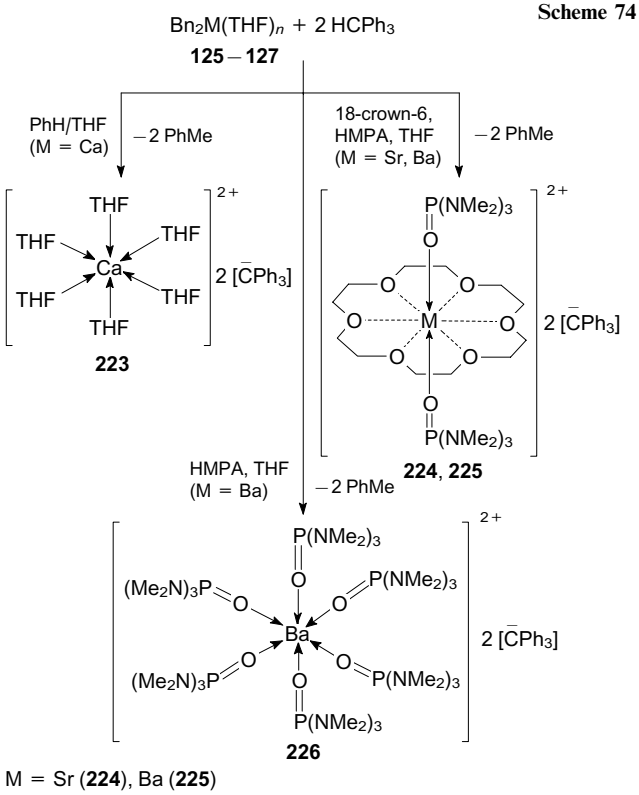
The first triphenylmethanide derivatives of Yb(II) were synthesized in 1995.[147] It was shown that when treating Yb metal with Ph$_3$CCl, the metal was oxidized to the divalent state to afford a mixture of complexes YbCl$_2$(THF)$_2$ and [Yb(THF)$_6$][CPh$_3$]$_2$ (**221**) (Scheme 73). With a prolonged reaction time, desymmetrization of the generated complexes occurred to give a heteroleptic triphenyl-chloride derivative **222**.

Later, triphenylmethanide complexes of heavy alkaline earth metals (Ca, Sr, Ba) were synthesized *via* transalkylation of Ph$_3$CH and Bn$_2$M(THF)$_n$.[109, 138, 148] The reaction of compound **125** with two equivalents of Ph$_3$CH in a benzene – THF mixture produces complex [Ca(THF)$_6$]$^{2+}$[CPh$_3$]$^-_2$ (**223**), which is a solvent-separated ion pair (Scheme 74).[109] To obtain bis(triphenylmethyl) derivatives of Sr and Ba, the

Scheme 73



Scheme 74

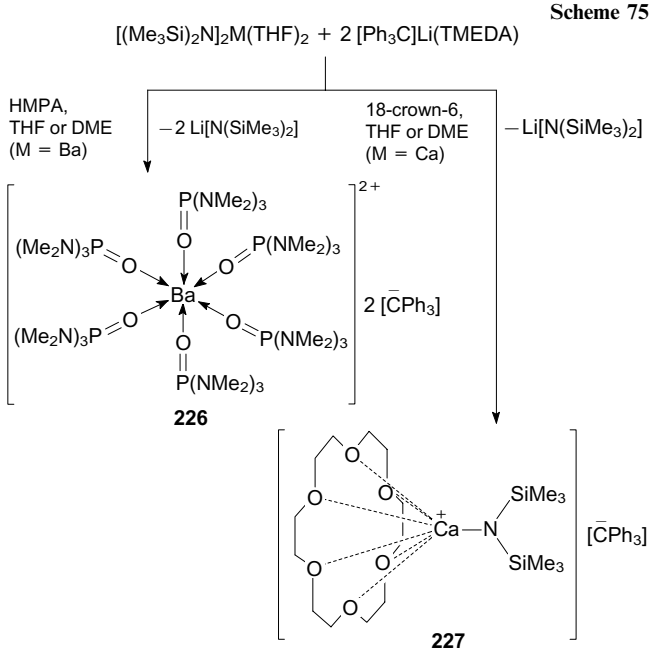


reaction of dibenzyl complexes **126** and **127** with Ph_3CH was carried out in the presence of HMPA or HMPA–18-crown-6 mixture to afford ionic complexes **224**,[148] **225**,[149] or **226**[138] (see Scheme 74).

Moreover, it was shown that complex **226** can be obtained by an exchange reaction between $[(Me_3Si)_2N]_2Ba(THF)_2$ and $[Ph_3C]Li(TMEDA)$ in THF or DMF–HMPA mixture (Scheme 75).[138]

The similar reaction of $[(Me_3Si)_2N]_2Ca(THF)_2$ with an excess amount of $[Ph_3C]Li(TMEDA)$ in the presence of 18-crown-6 resulted only in one amide moiety being substituted to yield complex $[\{(Me_3Si)_2N\}Ca(18\text{-crown-6})][CPh_3]$ (**227**). Alexander *et al.*[148, 149] also examined the possible approach to triphenylmethanide complexes of Sr and Ba *via* the substitution of an amide ligand upon treatment of complexes $[(Me_3Si)_2N]_2M(THF)_2$ with Ph_3CH in the presence of

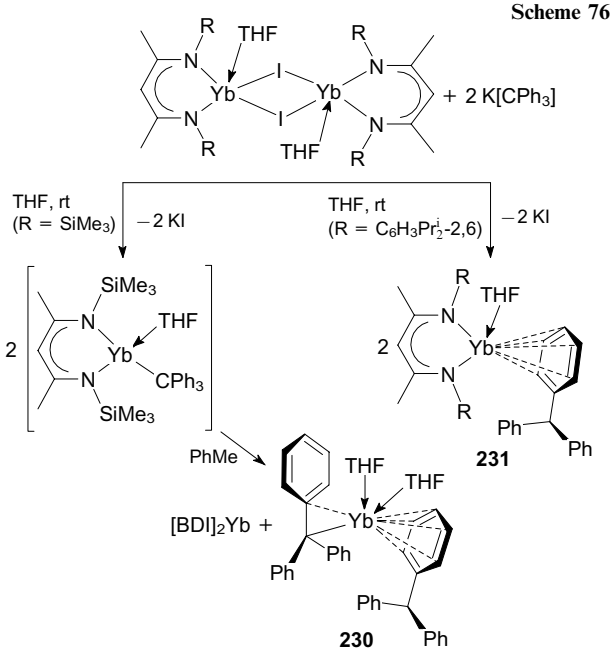
Scheme 75



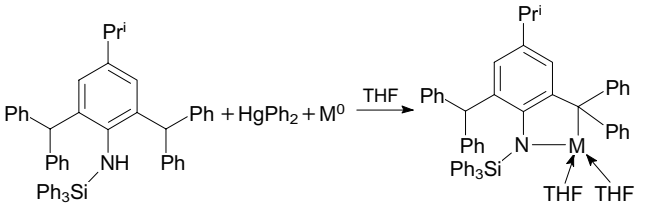
18-crown-6. The authors noted that a negligible difference in the acidity of amine $(Me_3Si)_2NH$ ($pK_a = 29.5$)[150] and triphenylmethane Ph_3CH ($pK_a = 30.6$)[136] allowed this reaction to proceed. However, the interaction was accompanied by the cleavage of the crown-ether C–O bonds affording dimeric ether-amide complexes **228**, **229**. Complexes **221** – **227** are solvent-separated ion pairs.

The first representatives of triphenylmethyl derivatives with the ligand–metal bond were complexes $[Ph_3C]_2Yb(THF)_2$ (**230**) and [BDI]Yb[CPh_3](THF) (**231**) obtained by exchange reactions of $\{[BDI]Yb(\mu\text{-}I)(THF)\}_2$ with $K(CPh_3)$ in THF (Scheme 76).[92] It should be noted that the nature of substituents at the nitrogen atoms of β-diketoiminate ligands ($SiMe_3$, $C_6H_3Pr^i_2$-2,6) significantly affect the stability of mixed-ligand Yb(II) triphenylmetha-

Scheme 76



Scheme 77



M = Ca (**232**), Yb (**233**), Eu (**234**) **232 – 234**

nides. For β-diketoiminate ligand bearing $SiMe_3$ substituents at the nitrogen atoms, the reaction resulted in symmetrization of the newly formed heteroleptic complex [BDI]Yb[CPh_3](THF) and produced a mixture of bis(triphenylmethyl) and bis(β-diketoiminate) derivatives. The use of β-diketoiminate ligand bearing bulkier $C_6H_3Pr^i_2$-2,6 substituents made it possible to isolate and characterize the structure of stable triphenylmethyl complex **231**. In a crystalline state, one of Ph_3C moieties of homoleptic complex **230** coordinates to the Yb(II) ion in the η^2-coordination mode, while the second one binds in the η^5-mode by *ortho*-, *meta*-, and *para*-carbons of one of the phenyl rings CPh_3. In mixed-ligand complex **231**, η^5-coordination of triphenylmethyl anion was also discovered.

In 2018, derivatives of Ca, Yb, and Eu **232 – 234**, bearing a dianionic amido-triphenylmethanide ligand, were obtained by the transmetallation reaction of Ca, Eu, and Yb metals with Ph_2Hg in the presence of a secondary amine [4-Pr^i-2,6-$(Ph_2CH)_2C_6H_2$]NH($SiPh_3$) (Scheme 77).[151] The authors suggest that the [4-Pr^i-6-$(Ph_2CH)C_6H_2N(SiPh_3)$-2-Ph_2C]$^{2-}$ dianion is generated by the proton abstraction from the amino group followed by metallation of the activated CH bond of the benzhydryl substituent $CHPh_2$ with a highly reactive intermediate [4-Pr^i-2,6-$(Ph_2CH)_2C_6H_2N(SiPh_3)$]M[Ph]. Complexes **232 – 234** feature η^3-coordination of the triphenylmethyl moiety to the metal ion. Along with the methanide carbon atom, *ipso*-carbons of two phenyl rings of the benzhydryl substituents are also involved in the meta – ligand interaction.

Activation of the benzhydryl group of the aryl substituent at the nitrogen atoms of an amidinate ligand was observed in the reaction of $PhSiH_3$ with [Amd^{Ar}]Sr[$N(SiMe_3)_2$] [Amd^{Ar} = *p*-TolC(NC_6H_2-Pr^i-4-$(CHPh_2)_2$-2,6)$_2$], which furnished complex **235**, containing dianionic amidinate-triphenylmethyl ligand (Scheme 78).[152]

5. The catalytic activity of alkyl complexes of Ln(II) and heavy alkaline earth metals

Alkyl derivatives of divalent lanthanides and heavy alkaline earth metals demonstrate not only unique reactivity but also high catalytic activity in a series of transformations of unsaturated substrates. These compounds proved to be effective catalysts for intermolecular hydrobenzylation, hydroamination, hydrosilylation, hydrophosphination, and hydrothiolation of alkenes and alkynes, are active in intermolecular cross-dehydrocoupling reactions between hydrosilanes and amines, and can initiate controlled polymerization of styrene.

5.1. Hydrofunctionalization of alkenes and acetylenes

Hydrofunctionalization reactions including the addition of the reactive E – H bonds across the multiple C=C and C≡C bonds of alkenes and acetylenes is an atom-economic synthetic approach to the formation of the carbon – heteroelement bonds. These reactions are accomplished due to the pronounced tendency of divalent lanthanide and heavy alkaline earth metal compounds to be readily involved in the σ-bond metathesis and the possibility of the subsequent insertion of the multiple C – C bonds into the metal–heteroelement bond.[34 – 37, 41]

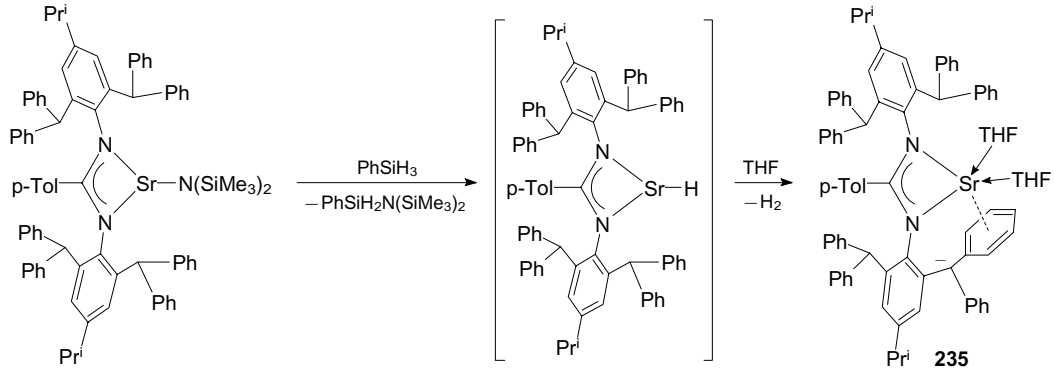
5.2. The C – C bond formation

Recently, [2,2′-(4-$MeC_6H_3NMe_2)_2$CH]$_2$Ca(THF)$_2$ **212** and [2,2′-(4-$MeC_6H_3NMe_2)_2$CH]$_2$M **213**, **214** complexes were shown to be effective and selective catalysts for hydrobenzylation of styrene with 2-methyl- and 2,6-dimethylpyridine.[142] A key step of these reactions includes the selective activation of the sp^3-bonds of the C – H methyl groups located at the *ortho*-position of the pyridine ring followed by the insertion of styrene into the forming M – C bond of the CH-activation product.

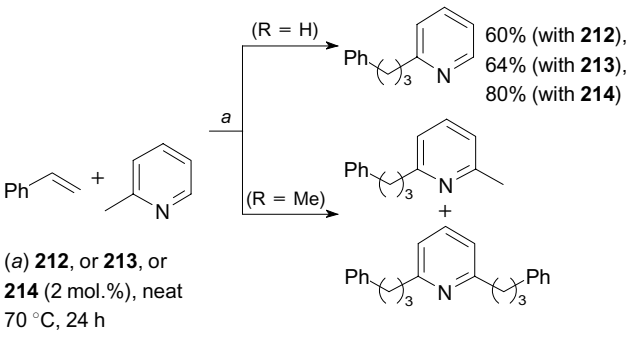
The addition of 2-methylpyridine across the styrene C=C bond in the presence of complexes **212 – 214** proceeds to give exclusively the linear anti-Markovnikov product [2-$(Ph(CH_2)_3C_5H_3N$ (Scheme 79).[142]

The use of Yb(II) complex **214** provides 80% conversion of substrates within 24 h at 70 °C, whereas Ca complexes **212** and **213** proved to be less active and under similar conditions gave the product of hydrobenzylation of styrene with 2-methylpyridine in yields of 60 and 64%, respectively. The authors noted that despite the higher reactivity of the sp^2-hybridized C – H bonds as compared to the sp^3-hybridized ones, the presence of complexes **212 – 214** led to the

Scheme 78



Scheme 79



exclusive formation of the products of styrene hydrobenzylation, whereas no hydroarylation products were detected.

Hydrobenzylation of styrene with 2,6-dimethylpyridine in the presence of complexes **212**–**214** also proceeds with excellent regioselectivity and affords linear anti-Markovnikov addition products (see Scheme 79).[142] The reaction of equimolar amounts of 2,6-dimethylpyridine and styrene ([St] : [Me_2Pyr] : [Cat] = 50 : 50 : 1), catalyzed with Yb(II) complex **214**, provides the formation of hydrobenzylation product within 24 h in 69% yield. Under similar conditions, Ca complexes **212** and **213** demonstrated slightly lower activity (55 and 50%, respectively). Moreover, Yb(II) complex **214** showed high chemoselectivity, giving the mono-addition product 2-Me-6-[$Ph(CH_2)_3$]C_5H_3N with 95% selectivity. With an excess of styrene ([St] : [2,6-Me_2Pyr] = 2.5 : 1) in the presence of Yb(II) complex **214**, the styrene adds across the C–H bonds of both methyl groups of 2,6-dimethylpyridine to give 2,6-[$Ph(CH_2)_3]_2C_5H_3N$ with 92% selectivity. The selectivity for bis(diphenylmethyl) Ca complexes **212** and **213** is significantly lower and regardless of the substrate ratio, a mixture of mono- and bis-addition products is formed.

The authors also noted that when using pyridine and 2-phenylpyridine as CH-substrates, complexes **212**–**214** proved to be inactive in the formation of the C–C bond.

5.3. Hydroamination of alkenes

The first examples of hydrofunctionalization reactions carried out with alkyl derivatives of heavy alkaline earth metals were intramolecular reactions of hydroamination–cyclization of aminoalkenes.

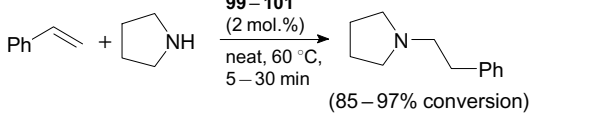
Arrowsmith *et al.*[102] investigated the catalytic acitivity of alkyl calcium complex [(C^5-$CH(SiMe_3)_2$)(dipp-BIAN)]Ca[$CH(SiMe_3)_2$]($THF)_2$ (**106**) in hydroamination–cyclization of terminal aminopentenes (Scheme 80). Cyclic pyrrolidines were formed in nearly quantitative yields (95–99%) in the presence of 0.5–2 mol.% of complex **106**.

In hydroamination–cyclization of an internal double bond of 2,2-diphenylhex-4-en-1-amine, complex **106** (5 mol.%) provides 95% conversion in 5 h. Complex **106** was much less active when using secondary 1-(1-allylcyclohexyl)-*N*-benzylmethylamine, bearing an additional benzyl group at the nitrogen atom, as 92% conversion was achieved in only 3.5 days.

Heteroleptic alkyl complexes of Ca, Sr, and Ba [N^-,N]M[$CH(SiMe_3)_2$]($THF)_n$ (**99**–**101**), containing an anilido-imine ligand, also allow for hydroamination–cyclization of 2,2-dimethylpent-4-en-1-amine.[93] Complexes of Ca **99** and Sr **100** proved to be most active giving rise to 2,4,4-trimethylpyrrolidine in quantitative yield in 2–3 min in the presence of 1 mol.% of the catalyst. The activity of the barium analogue **101** was significantly lower and under similar conditions, a high (96%) conversion was attained in 20 min.

It was also shown that complexes **99**–**101** are active in the intermolecular variant of catalytic hydroamination of styrene with pyrrolidine. However, these compounds proved to be inactive with benzyl amine. The reaction proceeded with 100% selectivity to afford solely the anti-Markovnikov product (Scheme 81). In this case, 85–97% conversion was achieved in 5 min in the presence of complexes **100**, **101**, and in 30 min for complex **99**.

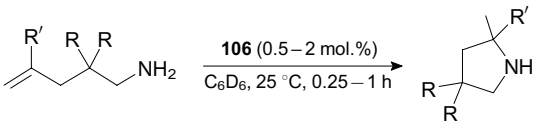
Scheme 81



Compounds [2,2′-(4-$MeC_6H_3NMe_2)_2CH]_2$Ca($THF)_2$ (**212**) and [2,2′-(4-$MeC_6H_3NMe_2)_2CH]_2$M (**213**–**215**) (M = Ca, Yb, Sm) containing pincer [$NC_{sp^3}N$] diphenylmethanide ligands show lower activity in the addition of pyrrolidine to styrene.[142] The quantitative formation of the anti-Markovnikov addition product in the presence of 2 mol.% of complexes **213**–**215** was reached in 72 h at 70 °C. However, this reaction can provide a similar result even at room temperature to afford quantitatively the single product $PhCH_2CH_2N(CH_2)_4$ in 5 days.

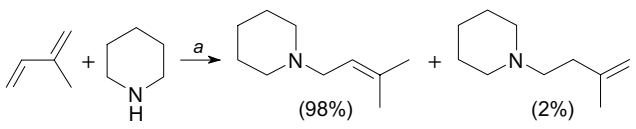
Brinkmann *et al.*[153] found that strontium complex [$(Me_3Si)_2CH]_2$Sr($Solv)_3$ **45** catalyzes the intermolecular hydroamination of styrenes and isoprene with piperidine. Complex **45** showed the highest activity in hydroamination of unsubstituted styrene providing 70% conversion in the presence of 5 mol.% of the catalyst in C_6D_6 at room temperature in just 10 min. For *para*-substituted styrenes 4-$RC_6H_4CH{=}CH_2$ (R = Me, OMe), the activity of complex **45** was markedly lower, and high values of conversion (90–95%) were reached in 35 and 90 min, respectively. In the case of isoprene hydroamination with piperidine, the activity of complex **45** was significantly lower and it took 72 h to reach 61% conversion (Scheme 82). However, the chemoselectivity of the reaction under the above conditions was high, and the product of 1,4-addition was formed with 98% selectivity.

Scheme 80



R′ = H: R = Me, cyclo-C_5H_9, Ph;
R′ = Me, R = Ph

Scheme 82

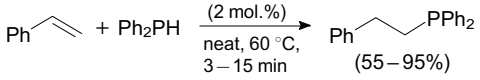


(*a*) **45** (1 mol.%), C_6D_6, 25 °C, 72 h

5.4. Hydrophosphination of alkenes and alkynes

Application of alkyl complexes of heavy alkaline earth metals in the catalytic intermolecular hydrophosphination of alkenes was first reported in 2013.[93] As catalysts, heteroleptic alkyl complexes of Ca, Sr, and Ba [N$^-$,N]M[CH(SiMe$_3$)$_2$](THF)$_n$ (**99**–**101**) bearing an iminoanilide ligand were used, which enable the addition of Ph_2PH to styrene to afford solely an anti-Markovnikov product in high yields (Scheme 83).

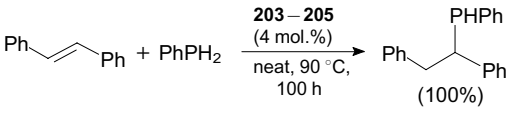
Scheme 83



Compounds [(4-Bu^{t}C$_6$H$_4$)$_2$CH]$_2$M(TMEDA) (M = Ca, Yb, Sm) (**203**–**205**) and [(4-Bu^{t}C$_6$H$_4$)$_2$CH]$_2$Sm(DME)$_2$ (**207**) also demonstrated their high efficiency as catalysts for intermolecular hydrophosphination of alkenes and alkynes.[140] When using Ph_2PH and $PhPH_2$ as substrates, hydrophosphination of styrene and α-Me-styrene in the presence of complexes **203**–**205** and **207** proceeds with a quantitative conversion of substrates to give anti-Markovnikov products with 100% selectivity (neat, 4 mol.%, 70 °C, 72 h). Here, in the case of primary phosphine $PhPH_2$, complexes **203**–**205** and **207** showed high chemoselectivity furnishing single addition products $PhCH_2CH_2P(H)Ph$ and $PhCH(Me)CH_2P(H)Ph$ with a selectivity of up to 86–90% at an equimolar ratio of substrates.

Moreover, complexes **203**–**205** were active in hydrophosphination of the internal C=C bond of *cis*- and *trans*-stilbenes.[140] Lanthanode(II) complexes **204** and **205** proved to be most effective, providing the quantitative formation of the hydrophosphination product (Scheme 84). Isostructural calcium complex **203** was much less active, and under similar conditions, conversion for *Z*-stilbene was 42%, while for *E*-stilbene it was as low as 16%.

Scheme 84



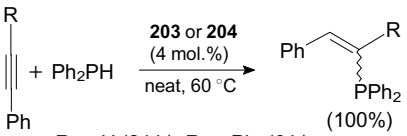
Complexes **203**, **204** allow for hydrophosphination of internal and terminal acetylenes with diphenylphosphine (Scheme 85).[140]

Using these complexes, terminal phenylacetylene reacts with Ph_2PH to afford quantitatively a mixture of *Z*,*E*-isomers $PhCH{=}CHPPh_2$ in approximately equal amounts in 24 h at 60 °C. Surprisingly, terminal diphenylacetylene PhC≡CPh is more reactive, and it takes only 6 h to reach quantitative conversion under similar conditions. In this case, complexes **203** and **204** demonstrate the highest stereoselectivity to yield the *E*-isomer of the resulting alkene with selectivities of up to 95 and 94%, respectively.

When using the most active Yb(II) complex **204**, it was first succeeded to carry out the sequential hydrophosphination of the C≡C triple bond with various phosphines (Scheme 86).

It was shown that *Z*,*E*-isomers $PhCH{=}CHPPh_2$ containing internal C=C bonds, formed in the first step of

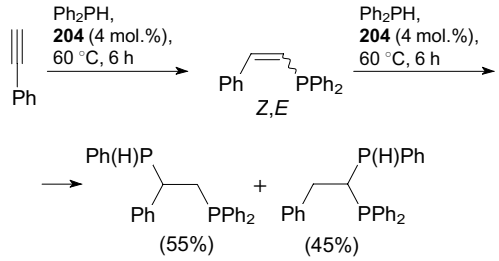
Scheme 85



R = H (24 h), R = Ph, (6 h)

R	Compound	*Z*/*E* isomers	R	Compound	*Z*/*E* isomers
H	**203**	48 : 52	Ph	**203**	94 : 6
H	**204**	43 : 57	Ph	**204**	95 : 5

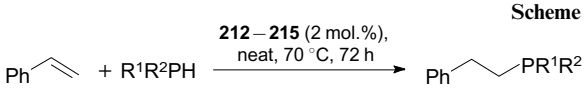
Scheme 86



phenylacetylene hydrophosphination with diphenylphosphine in the presence of Yb(II) complex **204**, can enter the subsequent reaction with primary phosphine $PhPH_2$ to give a mixture of 1,2- and 1,1-diphosphinoethanes.[140] At the same time, the authors failed to carry out double hydrophosphination of diphenylacetylene (tolane).

Complexes **212**–**215** also showed high activity in intermolecular hydrophosphination of styrene with primary and secondary phosphines to produce exclusively anti-Markovnikov addition products (Scheme 87).[142]

Scheme 87



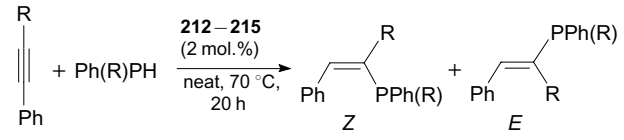
$R^1 = R^2$ = Ph, Cy; R^1 = Ph, R^2 = H

Aryl-substituted phosphines Ph_2PH and $PhPH_2$ were predictably more active as compared to aliphatic Cy_2PH. In addition to 100% regioselectivity, complexes **212**–**215** also provide high chemoselectivity. Being employed in styrene hydrophosphination with $PhPH_2$ with the use of equimolar amounts of substrates, complexes **212**–**215** give rise to the product of phenylphosphine monoalkylation with styrene with up to 96% selectivity [for Sm(II) **215**], whereas an excess of styrene (2.5 equiv.) under similar conditions leads to tertiary phosphine $PhP(CH_2CH_2Ph)_2$ in high yields (75–88%). Complexes **212**–**215** are also active in hydrophosphination of α-Me-styrene with both primary ($PhPH_2$) and secondary (Ph_2PH) phosphines. When using $PhPH_2$, the highest chemoselectivity was observed for Sm(II) complex **215**, which opens access to secondary phosphine $Ph(Me)CHCH_2P(H)Ph$ in the yield of up to 98% with the quantitative conversion of the alkene. Like diphenylmethyl derivatives **204** and **205**, complexes **212**–**215** allow for hydrophosphination of an internal C=C double bond of *cis*-stilbene to give the addition product $PhCH_2CH(Ph)P(H)Ph$ in 89–94% yield in 120 h at 100 °C. Interestingly, upon hydrophosphination of *cis*-stilbene with phenylposphine catalyzed by Ln(II) complexes

214 and **215**, the formation of the product of dehydrocoupling of phosphine PhHP–PHPh (14 and 7%, respectively) in considerable amounts was observed, whilst in the case of calcium analogues **212** and **213**, this did not happen.

Hydrophosphination of triple bonds of phenyl- and diphenylacetylenes with phosphines in the presence of complexes **212**–**215** proceeds significantly more readily as compared to hydrophosphination of double bonds, and quantitative conversion of substrates is reached in 20 h at 70 °C (Scheme 88).[142] The addition of Ph_2PH to PhC≡CH occurs against the Markovnikov's rule to furnish predominantly *Z*-isomers with 73–90% selectivity.

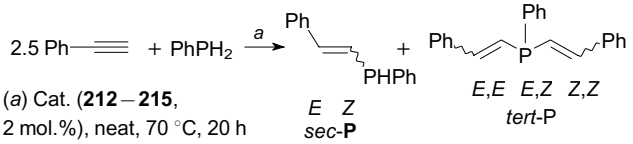
Scheme 88



R = Ph, H

The use of $PhPH_2$ in hydrophosphination of phenylacetylene at an equimolar substrate ratio afforded a mixture of mono- and bis-vinylated derivatives of phenylphosphine (Scheme 89).[142]

Scheme 89



(*a*) Cat. (**212**–**215**, 2 mol.%), neat, 70 °C, 20 h

Cat.	*sec*-P : *tert*-P	Cat.	*sec*-P : *tert*-P
212	29 : 71	**214**	40 : 60
213	49 : 51	**251**	55 : 45

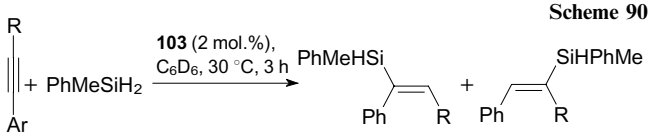
In the case of calcium complexes **212** and **213**, the use of excess phenylacetylene (2.5 equiv.) will increase the yield of products of double vinylation of $PhPH_2$ to 96 and 97%, respectively. Moreover, the presence of **213** leads to the predominant formation of *Z*,*Z*-$(PhCH{=}CH)_2PPh$ with the selectivity of up to 80%.

Phenyl- and diphenylphosphine add to tolane in the presence of compounds **212**–**215** with a quantitative conversion of substrates in 20 h at 70 °C.[142] Calcium complexes **212** and **213** demonstrated the highest stereoselectivity and provided *E*-isomers of alkenes (PhCH=CPh)PHPh and $(PhCH{=}CPh)PPh_2$ in yields up to 86 and 99%, respectively. When using Sm(II) analogue **215**, the *E*/*Z*-selectivity was slightly lower (up to 75 and 87% of *E*-isomer), while for Yb(II) complex **214**, *E*- and *Z*-isomers were formed in nearly equal amounts.

5.5. Hydrosilylation of alkenes and alkynes

The alkyl Sm(II) complex **103**, bearing a tetradentate β-diketoiminate ligand, was shown to exhibit high catalytic activity in hydrosilylation of internal 1-aryl-2-ethylacetylenes.[95] By the example of PhC≡CMe it was established that the secondary silane $PhMeSiH_2$ was most active in hydrosilylation of the internal C≡C bond. In the presence of 2 mol.% of **103**, the hydrosilylation products are formed in 94% yield (Scheme 90).

Scheme 90



R	Ar	Yield (%)	A : B	R	Ar	Yield (%)	A : B
Me	Ph	94	19 : 1	Me	C_6H_4F-4	84	11 : 1
Me	C_6H_4Me-4	91	17 : 1	Et	Ph	16	30 : 1
Me	C_6H_4Me-3	98	30 : 1	Me	2-Fu	4.5	–
Me	C_6H_4Me-2	72	30 : 1	Me	3-Fu	44	6 : 1
Me	C_6H_4OMe-4	90	12 : 1	Me	2-Th	19	2 : 1
Me	$C_6H_4NMe_2$-4	90	16 : 1	Me	3-Th	91	3 : 1

The activity of diphenyl-, phenyl-, and n-hexylsilanes was somewhat lower (conversions of 87, 47, and 31%, respectively), while with diethyl- and triphenylsilanes, complex **103** proved to be inactive. The authors noted that the said complex showed high stereoselectivity to produce predominantly *E*-isomers *via* the *syn*-addition of Si–H bonds across the C≡C bond, and also high regioselectivity (92–95%) since hydrosilylation products contained the silicon atom mainly at the aryl-substituted carbon atom $PhC(SiH_{3-n}R_n){=}C(H)Me$.

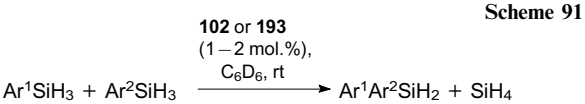
A large series of disubstituted acetylenes was used to study the effect of the nature of the aryl substituent in the acetylene substrate on the course of addition of $PhMeSiH_2$.[95] In the case of ArC≡CMe, in the presence of 2 mol.% of **103** the yields of the hydrosilylation products in 3 h at 30 °C in C_6D_6 reached 72–98%, whereas for PhC≡CEt, containing more bulky ethyl substituent, conversion was as low as 16%. It turned out that for furanyl- and thienyl-substituted acetylenes, the position of the heteroatom in the aromatic ring dramatically influences the reactivity. Thus, with complex **103**, the conversion values of 44 and 91%, respectively, were achieved. For their 2-substituted analogues, the rate of $PhMeSiH_2$ hydrosilylation was significantly lower and within the same period, the hydrosilylation products were formed in yields of 5 and 19%, respectively. Such decrease of reactivity can be attributed to the possibility of the O and S atoms to coordinate to the Sm(II) ion, thereby blocking the reactive site of the catalytically active species. Here, in all cases, *syn*-addition occurs to give only *E*-isomers.

It must be pointed out that Yb(II) complex **102** is inactive in hydrosilylation of acetylenes.[94,95] It turned out that even in the presence of acetylenes complex **102** promotes metathesis of primary arylhydrosilanes $ArSiH_3$ furnishing SiH_4 and Ar_2SiH_2. Liu *et al.*[94] showed that metathesis of silanes $ArSiH_3$, catalyzed by complexes **102** and **193**, can be used as a convenient approach to synthesize secondary silanes Ar_2SiH_2 (Scheme 91).

A series of symmetrical (Ar_2SiH_2) and unsymmetrical ($Ar^1Ar^2SiH_2$) silanes was obtained in yields from 37 to 99% in 15–45 min in the presence of 2 mol.% of complexes **102** and **193**.

Complexes **212**–**215**, bearing tridentate diphenylmethanide ligands, were shown to be effective catalysts for hydrosilylation of alkenes and acetylenes with phenylsilane.[142] In particular, these complexes demonstrated similar catalytic

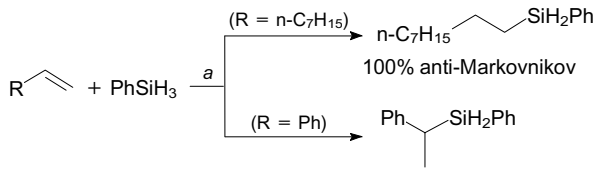
Scheme 91



$Ar^1 = Ar^2$	Yield (%)	*t*, min	Ar^1	Ar^2	Yield (%)	*t*, min
Ph	91	15	Ph	C_6H_4Cl-4	78	5
C_6H_4Ph-4	90	15	Ph	C_6H_4F-4	77	5
C_6H_4Me-4	87	15	Ph	C_6H_4OMe-4	67	45
C_6H_4Me-2	39	15	Ph	$C_6H_4NMe_2$-4	71	45
C_6H_4OMe-4	87	15	C_6H_4Cl-4	C_6H_4Me-4	97	5
$C_6H_4NMe_2$-4	18	15	C_6H_4Cl-4	C_6H_4OMe-4	86	5
C_6H_4F-4	87	3	C_6H_4Cl-4	$C_6H_4NMe_2$-4	88	5
C_6H_4Cl-4	83	1	C_6H_4F-4	C_6H_4Me-4	91	5
			C_6H_4F-4	C_6H_4OMe-4	84	5
			C_6H_4F-4	$C_6H_4NMe_2$-4	87	20
			C_6H_4Cl-4	C_6H_4F-4	45	5
			C_6H_4OMe-4	$C_6H_4NMe_2$-4	37	45

activity in the addition of $PhSiH_3$ to non-1-ene and styrene and provided a quantitative conversion of substrates in 1.7 – 2.5 h in the presence of 2 mol.% of catalysts (C_6D_6, 20 °C; see Scheme 90). Regioselectivity of the catalytic formation of the Si – C bond in the presence of complexes **212** – **215** is governed by the nature of both the substrate and the metal. In the case of non-1-ene, all complexes provided an exclusive formation of a linear addition product n-$C_9H_{17}SiH_2Ph$, whereas for styrene only branched addition product $PhCH(Me)SiH_2Ph$ was obtained (Scheme 92).

Scheme 92

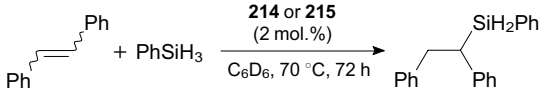


(*a*) Cat (**212** – **215**, 2 mol.%), C_6D_6, rt, 1.7 – 2.5 h

Hydrosilylation of α-Me-styrene catalyzed by complexes **212** – **215** occurred much more slowly: 65 – 75% conversion was achieved in only 40 h at 20 °C. Complexes of Ln(II) **214** and **215** exhibited high regioselectivity in this reaction and produced the Markovnikov product $PhC(Me)_2SiH_2Ph$ with a selectivity of 99 and 96%, respectively.[142] Regioselectivity of the reaction in the presence of Ca complexes **212** and **213** was slightly lower, and the Markovnikov selectivity was 75%. Raising the temperature to 70 °C provides the quantitative conversion of substrates in 10 – 18 h; however, at the same time regioselectivity decreases. When using Ln(II) complexes **214** and **215**, a mixture of the branched [$PhC(Me)_2SiH_2Ph$] and linear [$PhCH(Me)CH_2SiH_2Ph$] products is formed in a ratio of 80 : 20 [for Yb(II) **214**] and 85 : 15 [for Sm(II) **215**], while with calcium complexes **212** and **213**, the Markovnikov and anti-Markovnikov products are produced in nearly equal amounts (53 : 47 for **212**; 58 : 42 for **213**).

Complexes of Ln(II) **214** and **215** also enable the addition of $PhSiH_3$ across an internal C=C double bond.[142] Hydrosilylation of *cis*- and *trans*-stilbenes $PhSiH_3$ requires more harsh conditions as compared to terminal

Scheme 93

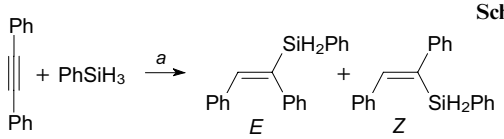


cis- or *trans*- **214** (88%), **215** (76%)

alkenes and produces the addition product in yields of 88% and 76%, respectively (Scheme 93).

Complexes **214**, **215** also catalyze the $PhSiH_3$ addition across an internal double bond of tolane and under similar conditions afford a mixture of (*E*,*Z*)-isomers $PhCH{=}C(Ph)SiH_2Ph$ in yields of 92% and 80% with an *E*-isomer content of 80% and 69% respectively (Scheme 94).[142]

Scheme 94



(*a*) **214** or **215** (2 mol.%) C_6D_6, 70 °C, 72 h

Complex	Yield (%)	*E* : *Z*
214	88	80 : 20
215	76	69 : 31
212 or **213**	0	

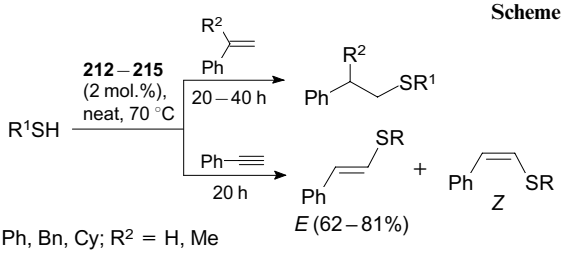
It is noteworthy that calcium complexes **212**, **213** proved to be inactive in the catalysis of the $PhSiH_3$ addition to stilbene and tolane under the above-mentioned conditions. As in the case of heteroleptic Yb(II) complexes **102** and **193**, the use of calcium complexes **212**, **213** led to metathesis of $PhSiH_3$ as a predominating reaction, which gave an equimolar mixture of SiH_4 and Ph_2SiH_2, while unsaturated substrates did not react. This provided a 65% conversion of $PhSiH_3$ (C_6D_6, 70 °C, 72 h).

5.6. Hydrothiolation of alkenes and alkynes

To date, activity of alkyl derivatives of Ln(II) and heavy alkaline earth metals in catalysis of intermolecular hydrothiolation of alkenes and alkynes remains unexplored. It has recently been shown that complexes **212** – **215** catalyze the addition of phenyl-, benzyl-, and cyclohexylthiols to styrene (Scheme 95).[142]

In all cases, hydrothiolation proceeds to produce anti-Markovnikov products. The nature of the substituent in the sulfur-containing substrate is crucial for the yields of the hydrothiolation products. Phenylthiol PhSH proved to be the most active substrate in the reaction with styrene, and the quantitative yield of the product in the presence of **212** – **215** was achieved in 20 h at 70 °C. The addition of BnSH and CySH to styrene under similar conditions proceeds much more slowly, and high conversion of substrates

Scheme 95



R^1 = Ph, Bn, Cy; R^2 = H, Me

(95 – 99% for BnSH; 63 – 90% for CySH) was observed in only 40 h. Hydrothiolation of α,α-disubstituted alkene (α-Me-styrene) with PhSH can also be carried out in the presence of complexes **212** – **215** to afford the anti-Markovnikov product in 56 – 74% yield. However, the authors mentioned that complexes **212** – **215** are inactive in the addition of the aforementioned thiols across the internal C=C double bonds of *cis*- and *trans*-stilbenes.

Moreover, complexes **212** – **215** displayed high catalytic activity in hydrothiolation of the terminal C≡C triple bond of phenylacetylene with the same series of thiols.[142] Quantitative conversion of reactants was achieved in 20 h at 70 °C (see Scheme 92). The complexes demonstrated absolute regiospecificity providing the formation of exclusively anti-Markovnikov products. In all cases, a mixture of *cis*- and *trans*-isomers with predominantly (*E*)-isomer (62 – 81%) was obtained. At the same time, complexes **212** – **215** proved to be completely inert in hydrothiolation of the internal C≡C bond of tolane.

5.7. Cross-dehydrocoupling of hydrosilanes with amines

Sadow and co-workers[84] investigated the reactivity Ln(II) bis(alkyl) complexes **57** and **58** $[(Me_2SiH)_3C]_2M(THF)_2$ (M = Yb, Sm), and also **61** and **62** $[(Me_2SiH)_3C]_2M(NHC)$ (M = Yb, Sm) in cross-dehydrocoupling of silanes with amines proceeding with the formation of the Si – N bond and release of H_2. Complexes **61** and **62**, bearing the coordinated NHC-carbene ligands, were shown to be effective catalysts for the cross-dehydrocoupling of primary and secondary silanes with primary and secondary amines (Scheme 96). At the same time, their THF-coordinated analogues **57** and **58** turned out to be inert in these transformations.

Scheme 96

$R^1R^2SiH_2 + HNR^3R^4 \xrightarrow[C_6D_6,\ 25\ ^\circ C]{\textbf{61 or 62}\ (5-10\ mol.\%)} R^1R^2HSi-NR^3R^4 + H_2$

R^1	R^2	R^3	R^4	Time, h	Yield (%)
Ph	H	H	Pr^i	0.1	63
Ph	H	H	Bu^t	15	92
Ph	Me	H	Bu^t	4	87
Ph	Me	Et	Et	4	92
Ph	Ph	H	Pr^i	15	88
Ph	Ph	H	Bu^t	15	87
Ph	Ph	Et	Et^t	15	82

Complexes **61** and **62** give rise to products of the Si – N-coupling between $PhSiH_3$ and primary amines in nearly quantitative yields just in several minutes at room temperature. With secondary silanes and secondary amines, the Si – N-dehydrocoupling proceeds much more slowly, and high conversions (75 – 93%) are attained in 15 hours. In this case, depending on the initial ratio of substrates, complexes **61**, **62** provide selective synthesis of products of dehydrocoupling of a primary silane with several (1 – 3) amine molecules, or dehydrocoupling of a primary amine with one or two silane molecules.[84]

A similar effect of the Lewis base coordinated to the calcium ions in bis(alkyl) derivatives **44**, **54**, and **55** $[(Me_3Si)_2CH]_2Ca(Solv)_n$ [Solv = THF, $Ph_3P(O)$, NHC-carbene] on activity in catalytic cross-dehydrocoupling of $PhSiH_3$ with Pr_2iNH has been demonstrated.[81] The highest activity was observed for complex **55** bearing carbene ligands. With 5 mol.% **55** (C_6D_6, 25 °C, 12 h), the yield of the Si – N dehydrocoupling products reached 98%. With complexes **44** and **54**, bearing coordinated molecules of THF or Ph_3PO, conversion of substrates in 8 h was 10 and 5%, respectively.

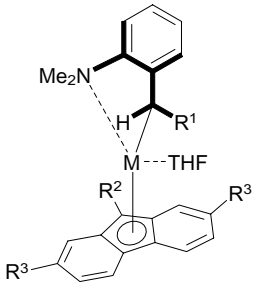
5.8. Polymerization of alkenes

The first examples of the use of bis(alkyl) complexes of heavy alkaline earth metals in polymerization of alkenes were published by Harder and co-workers[124, 125] in the early 2000s. It was demonstrated that bis(*o*-dimethylaminobenzyl) complexes $[o\text{-}Me_2NC_6H_4CH(SiMe_3)]_2M(THF)_2$ [M = Ca (**165**), Sr (**166**)] are active initiators for anionic polymerization of styrene and provide quantitative conversion of 1000 equivalents of styrene in 30 min at room temperature. The resulting polymers were characterized by an atactic microstructure, relatively high molecular mass ($M_n = 1.093 \times 10^5$), and relatively low polydispersity index [1.369 (**165**), 1.218 (**166**)]. The good correlation between experimental and calculated molecular mass values and the possibility of post-polymerization upon the addition of new portions of styrene at regular intervals while maintaining the activity of the catalysts argues in favour of the mechanism of living polymerization.

Harder and co-workers[48, 127 – 130] found that heteroleptic half-sandwich *o*-dimethylaminobenzyl complexes of Ca and Yb(II) **172** – **179** bearing fluorenyl ligands also initiate living polymerization of styrene and afford polystyrene of predominantly syndiotactic structure. In the presence of calcium complex **172**, polymerization of styrene at 20 °C gives a polymer containing up to 91.2% of *r*-dyads and 83.1% of *rr*-triads.[127] Stereocontrol can be improved by carrying out polymerization at a reduced temperature (at −20 °C r = 92.6%, rr = 85.7%). A Yb(II)-analogue **173** of this complex demonstrates somewhat lower stereocontrol (r = 82%, rr = 67%), which was attributed by the authors to the rapid inversion of stereocentres during polymerization.

A study[130] considers the catalytic activity of half-sandwich fluorenyl complexes **174** – **176**, **178**, and **181** in styrene polymerization. It was shown that an increase in the steric loading in positions 2 and 7 of the fluorenyl ligand leads to the increase in the degree of stereocontrol of styrene polymerization. The use of complex **181** bearing Bu^t substituents in the positions 2,7 of the fluorenyl anion gives rise to a syndiotactic polymer having up to 87% of *r*-dyads. The introduction of more bulky substituents CMe_2Ph and $CMePh_2$ (compounds **174** and **175**) enhance the content of syndiotactic units up to 88 and 92%, respectively. A further increase in the volume of the fluo-

Structures 172 – 182



172 – 182

$R^1 = R^2 = SiMe_3$, R^3 = H:
M = Ca (**172**), Yb (**173**);
M = Ca: $R^1 = R^2 = SiMe_3$:
$R^3 = CMe_2Ph$ (**174**), $CMePh_2$ (**175**),
$CMe(C_6H_4Bu^t\text{-}4)_2$ (**176**);
R^1 = Me, $R^2 = SiMe_3$, R^3 = H (**177**);
$R^1 = SiMe_3$: $R^2 = SiEt_3$,
$R^3 = CMe_2Ph$ (**178**);
$R^2 = Si(SiMe_3)_3$, R^3 = H (**179**);
R^1 = H, $R^2 = SiMe_3$, $R^3 = Bu^t$ (**181**);
$R^1 = R^3$ = H, $R^2 = (CH_2)_2NMe_2$ (**182**)

renyl ligand by introducing $CMe(C_6H_4Bu^t\text{-}4)_2$ substituents (**176**) into positions 2,7 or by replacing $SiMe_3$ group in the position 9 with $SiEt_3$ (**178**) does not significantly improve the degree of syndiotacticity of the resulting polystyrene. The authors noted that complex **182** bearing the fluorenyl ligand with a donor $CH_2CH_2NMe_2$ moiety in the position 9 proved to be completely inactive in styrene polymerization.

5.9. Hydrogenation of alkenes

Alkyl complexes of Ln(II) and heavy alkaline earth metals are both precusors and intermediates in the catalytic hydrogenation of alkenes. Several studies have demonstrated that the reaction of alkyl complexes with molecular hydrogen is accompanied by hydrogenolysis of the M – C bonds, furnishing the corresponding hydrides, which can further add across the multiple bonds of alkenes to give novel alkyl derivatives.[62–66, 122, 123] However, only a few examples of the application of alkyl complexes in catalytic hydrogenation of alkenes and alkynes are known to date.

Shi *et al.*[66] found that benzyl complex $[Tp^{Ad,Pr^i}]Ca(CH_2C_6H_4Me\text{-}4)(THP)$ (**157**) is an effective catalyst for hydrogenation of terminal and internal alkenes with molecular hydrogen [C_6D_6, 40 °C, $P(H_2)$ = 10 atm]. Complex **157** was the most effective in the hydrogenation of terminal alkenes providing the quantitative conversion for styrene, 1,1-diphenylethene, 1-hexene, and trimethyl(vinyl)-silane in 1 h, and for α-Me-styrene and *trans*-stilbene in 3 and 4 h, respectively. In the hydrogenation of internal alkenes, the activity of complex **157** was significantly lower. Hydrogenation of 2-octene to octane under catalysis with complex **157** allows attaining conversions of 31 and 90% in 24 and 72 h, respectively. Hydrogenation of cyclic substrates (norbornene and *cis*-cyclooctene) containing internal C=C bonds in the presence of **157** proceeds in 7 and 24 h to afford hydrogenation products with 97 and 95% conversions, respectively. For non-conjugated 4-vinylcyclohexene, complex **157** provides the selective hydrogenation of the terminal C=C bond to give 4-ethylcyclohex-1-ene, with the internal C=C bond of the cyclohexene ring remaining intact. The authors note that compound **157** is active in hydrogenation of the internal bond of cyclohexene, however, one failed to attain high conversion values (4%, 24 h; 22%, 120 h), and with 2-ethyl-1-butene, this complex proved to be completely inactive.

Dimeric calcium complex $\{[Amd]Ca\}_2[\mu\text{-}PhCHCHPh]$ (**163**), bearing bridging dianionic dibenzyl ligand, was shown to be an active catalyst in the hydrogenation of diphenylacetylene.[122] In the presence of 10 mol.% of complex **163**, hydrogenation of diphenylacetylene with molecular H_2 (6 atm.) affording 1,2-diphenylethane occurs in 48 h in C_6D_6 at 80 °C with quantitative conversion.

6. Conclusion

Advances in the synthesis of alkyl derivatives of divalent rare earth and heavy alkaline earth metals, achieved over the past two decades, indicate that these compounds are no longer elusive exotics. Such a breakthrough became possible due to the development of our understanding of the relationship between structure, stability, and reactivity, understanding the ways of stabilization of these highly reactive compounds, the way to ensure their kinetic stability. A notable contribution has been made to the concept of molecular design thus offering great potential to control the reactivity of rare earth complexes *via* constructing the ligand systems and coordination sphere of a metal ion.

However, much more meaningful conceptual generalizations and conclusions follow from the analysis of achievements made in the field of catalytic application of these compounds, which will undoubtedly influence the paradigm of homogeneous catalysis, enriching it with new approaches. Not long ago, it was difficult to imagine that the formation of C – C and C – E bonds could be realized without involving cross-coupling reactions, which include the steps of oxidative addition and reductive elimination and require the use of transition metals species with several stable oxidation states.[154–156] The catalytic transformations of unsaturated hydrocarbons that have been carried out using Ln(II) and heavy alkaline earth metal complexes, for which the possibility of substrate activation due to the usual back-donation of d-electrons to its antibonding orbitals is excluded, raise the issue of the implementation of a fundamentally different mechanism of activation of multiple C – C bonds. As Harder and co-workers[157] have shown in their pioneering study, M(II) cations, being hard Lewis acids, can activate the multiple bonds of alkenes due to electrostatic interaction, thereby causing polarization of the π-electron density of the alkene and enabling the subsequent attack of the nucleophile. Novel approaches to the formation of C – C and C – E bonds can be based on the ability of the alkyl derivatives of rare- and alkaline earth metals to selective activation of C – H bonds, insertion of multiple C – C bonds into M – C bonds, and σ-bond metathesis. The use and combination of various catalytic approaches to solving the current challenges of synthetic organic chemistry will significantly speed up its development. On the other hand, comparison of catalytic behaviour of complexes of divalent lanthanides and their structural analogues that contain the ions of heavy alkaline earth metals with similar radii will help to have a deeper insight into regularities of homogeneous catalysis and particularly to identify the factors (the ionic radius or electron structure of the central ion) responsible for the catalytic activity and selectivity of reactions promoted by these compounds.

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7. List of acronyms

The following acronyms were used in the review:

Ad — adamantan-1-yl,
Amd — *N*,*N*′-bis(2,6-diisopropylphenyl)pivalamidinate,
BDI — β-diketoiminate,
Bn — benzyl,
Carb — 1,3,6,8-tetra(*tert*-butyl)carbazole,
Cp — 1,3-cyclopentadienyl,
Cp^{BIG} — 1,2,3,4,5-pentakis(4-*tert*-butyl)-1,3-cyclopentadienyl,
Cy — cyclohexyl,
DFT — density functional theory,
diox — 1,4-dioxane,
DiPeP — 2,6-diisopentylphenyl,
DME — 1,2-dimethoxyethane,
Fu — furyl,
hpp — 1,3,4,6,7,8-hexahydro-2*H*-pyrimido[1,2-a]pyrimidinyl,
$(Me_3TACD)H$ — 1,4,7-trimethyl-1,4,7,10-tetraazacyclodecane,

NHC-carbene — 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene,
NH_2Dipp — 2,6-diisopropylaniline,
PMDETA — N,N,N',N'',N'''-pentamethyldiethylenetriamine,
Py — pyridine,
TACD — 1,3,5,7-tetramethyl-1,3,5,7-tetraazocyclodecane,
Th — thienyl,
THP — tetrahydropyran,
TMEDA — N,N,N',N'-tetramethylethylenediamine,
TMTA — 1,3,5-trimethyl-1,3,5-triazine,
Tp — tris(pyrazolyl)borate,
Tp^{Ad,Pr^i} — hydrotris(3-adamantyl-5-isopropylpyrazolyl)borate.

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